PB85-221661

Survey of Carbon Tetrachloride Emission Sources

Radian Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jul 85

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-85-018
July 1985

PB85-221661

Air

EPA

Survey of Carbon Tetrachloride Emission Sources

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

NESHAP

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/3-85-018	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Survey of Carbon Tetrachloride Emission Sources		5. REPORT DATE July 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. H. Howle, S. A. Shareef, J. A. Kowalski Radian Corporation - Post Office Box 13000 Research Triangle Park, North Carolina 27709		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Air Quality Planning and Standards Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. EPA Contract 68-02-3816
12. SPONSORING AGENCY NAME AND ADDRESS DAA for Air Quality Planning and Standards Office of Air and Radiation U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

Emission Standards and Engineering Division Lead Engineer: Robert B. Lucas

16. ABSTRACT

This document contains information on sources, current emission rates, current emission controls, and cost estimates for additional emission reductions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Pollution Control Organic Chemical Industry Carbon Tetrachloride	Air Pollution Control	13B

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 226
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/3-85-018

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Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

July 1985

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1.0 SUMMARY

The objective of this study is to identify all major sources of carbon tetrachloride (CCl_4) emissions in the United States and to provide quantitative estimates of those emissions. Information on the identified CCl_4 sources includes: source location, CCl_4 emission rates, and present control technologies. The information collected in this study was used to develop a CCl_4 material balance and to estimate costs to control sources that are not presently well controlled. The emissions information will also be used by the Environmental Protection Agency (EPA) to estimate human exposure to CCl_4.

In this study information requests were sent to all producers of CCl_4 and all identified major uses of CCl_4 under authority of Section 114 of the Clean Air Act. Plant specific emissions information was obtained for all CCl_4 production and about 95 percent of the 1983 CCl_4 use. An additional 2.7 percent of the use was in grain fumigants. This use is expected to cease by the end of 1985. No specific emission information was obtained on the remaining 2.3 percent of CCl_4 use, however, the companies using all but 660 Mg were identified. Therefore, there are no remaining unidentified large uses of CCl_4.

1.1 INDUSTRY DESCRIPTION

Carbon tetrachloride (CCl_4) is produced as a product by six companies at nine facilities. The total estimated 1983 production of CCl_4 at these facilities is 275,350 megagrams (Mg). Carbon tetrachloride is also formed as a byproduct in the production of ethylene dichloride (EDC). Byproduct CCl_4 formed in EDC production is not sold as product CCl_4. It is either disposed of, sold as crude byproduct, or carried along in the product EDC as an impurity.

In 1983, U.S. CCl_4 sales totalled 258,096 Mg. An additional 10,934 Mg was used captively by CCl_4 producers. Therefore, total U.S. CCl_4 consumption in 1983 is estimated to be 269,030 Mg (this value may not include 3,200 Mg in exports). About 93.4 percent of the CCl_4 was consumed in chlorofluro-carbon (CFC) 11 and 12 production, 2.7 percent was consumed as grain fumigant, 0.5 percent was used in chlorine production, 1.5 percent was used in pesticide production, 0.09 percent was used in pharmaceutical production, and the remaining 1.8 percent was consumed mainly in miscellaneous chemical processes. Registration for the use of CCl_4 as a grain fumigant has recently been cancelled by the EPA.

1.2 EMISSION ESTIMATES

The total estimated emissions from production and use of CCl_4 in 1983 are 3,285 Mg excluding emissions from grain fumigants. The largest sources of emissions were from CCl_4 production (898 Mg), use of CCl_4 in chlorine production (355 Mg), and use of CCl_4 in pesticide production (1,200 Mg). The estimated emissions from all sources are presented in Table 1-1. Estimates presented for CCl_4 production, CFC production, EDC production, chlorine production, pesticide production and miscellaneous production processes are based on companies' responses to EPA information requests. These specific company responses accounted for all production of CCl_4 and about 95 percent of CCl_4 use. The responses included emission estimates for process vents (estimated at full plant capacity), loading/handling operations, equipment opening losses, pressure relief valve discharges, and secondary streams. The plants also provided equipment count data for equipment in CCl_4 service. Total volatile organic compound (VOC) emissions from equipment leak sources were calculated by applying SOCMI VOC equipment leak emission factors to the supplied equipment counts. CCl_4 emissions were estimated by applying the fraction of CCl_4 in the stream for each piece of equipment to the calculated VOC emissions. (Actual test data were provided by one plant for CCl_4 equipment leak emissions.) Emissions from storage tanks were estimated by using AP-42 equations and company supplied storage tank data. Methods for estimating these emissions are described in Appendix B.

TABLE 1-1. EMISSIONS FROM THE PRODUCTION AND USE OF CCl_4

Process	1983 Production/Consumption (Mg/yr)	CCl_4 Emission[a] (Mg/yr)
CCl_4 Production	275,350	898
CFC Production	251,216	132
Grain Fumigants	7,160	-[b]
EDC Production	N/A	71
Chlorine Production	1,406	355
Pesticide Production	4,105	1,200
Pharmaceutical Manufacturing	231	26
Miscellaneous Production Processes	2,042	374
Other Uses	2,870	Not estimated
Distribution	N/A	9
POTW	N/A	220
TOTAL	---	3,285

N/A - Not Applicable

[a] Emission estimates obtained from plant specific Section 114 responses total 2,200 Mg. This value should be used for comparison with potential reductions presented in Table 1-2.

[b] Registration of CCl_4 in grain fumigants has been cancelled by the EPA. This use is expected to cease by the end of 1985.

1.3 REGULATORY REQUIREMENTS

Carbon tetrachloride emissions are not specifically controlled by any Federal regulations under the Clean Air Act. However, facilities producing ethylene dichloride are generally well controlled as a result of the national emission standards for hazardous air pollutants (NESHAP) for vinyl chloride (VC). The VC NESHAP generally requires control of process vent emission at EDC plants by incineration. The VC standard also requires a formal program for control of fugitive VC emissions.

State and District regulations for VOC are the source of regulatory requirements at most facilities. Louisiana and Texas both have VOC regulations requiring control of process vent emission by incineration. However, in Texas vent streams emitting less than 110 kg/hr are exempt. There is no such exemption in Louisiana. However, the control requirements can be waived if the VOC emissions are less than 91 Mg/yr, will not support combustion or cause economic hardship. Also, the Bay Area Air Quality Management District (BAAQMD) in California requires recovery, incineration, or containment of process vessel depressurization emissions.

Equipment leak emissions are presently regulated by the BAAQMD and the South Coast Air Quality Management District (SCAQMD) in California. BAAQMD regulations require repair of leaks greater than 10,000 ppm VOC within 15 days for accessible nonessential valves and flanges. For essential valves and flanges, leaks must be minimized within 15 days and repaired within six months. The first inspection was required prior to January 1, 1984, and subsequent inspections are required at least annually. Valves and flanges that are identified as leaking must be inspected quarterly. The SCAQMD requires annual inspection for leaks (10,000 ppm VOC) from pumps, valves, and flanges, and quarterly inspection for compressors. Repair is required at the next scheduled turnaround for pumps and compressors and immediately for valves and flanges. Open lines are required to be capped and safety relief valves must be protected by a rupture disc or vented to a control device.

Both Texas and Louisiana have recently enacted equipment leak regulations with a final compliance date of December 31, 1987. The Texas regulations apply only in Harris County. Requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and valves in liquid service, monthly leak detection for compressor seals and valves in gas service, and weekly visual inspection of pump seals. Repair or reasonable measures to minimize identified leaks is required within 15 days. Also, open-ended lines are required to be capped.

Texas, Louisiana, Illinois, Michigan, the BAAQMD, and SCAQMD all have regulation for VOC emissions from storage tanks. CCl_4 storage tanks greater than 40,000 gallons are required to be controlled by an internal floating roof with a primary seal, an external roof with both primary and secondary seals, a refrigerated condenser or a combustion technique. In New Jersey, these controls are required for tanks greater than 300,000 gallons.

VOC emissions from loading are regulated by Texas, Louisiana, Michigan, and Illinois. Texas and Louisiana require vapor collection and recovery or disposal for facilities loading greater than 20,000 gal/day (40,000 gal/day for existing facilities in Louisiana). Michigan and Illinois only require submerged fill. Ship and barge loading are exempt in Texas and Louisiana.

1.4 ADDITIONAL CONTROL OF CCl_4 EMISSIONS

Emissions of CCl_4 from chemical plants producing or using CCl_4 can be reduced by various technically feasible controls. Process vent emissions can be controlled by incineration or carbon adsorption. Fugitive emissions can be reduced through a combination of leak detection and repair programs and application of equipment control devices. Storage tank emissions can be reduced by installation of floating roofs in fixed roof tanks. Where floating roofs are not technically feasible (i.e. horizontal tanks or extremely small diameter tanks), a refrigerated condenser can be used for control of storage emissions. Loading emissions can be controlled by venting displaced vapors to an incinerator.

Costs were estimated for the above control techniques for all emission sources which are not presently well controlled. These costs estimates are based on the information provided in the company responses on the emission stream and process equipment parameters. It is estimated that about 1,500 Mg/yr CCl_4 emissions can be controlled by the application of control techniques on process vent, fugitive, storage tanks, and handling emissions. This represents an overall emission reduction of about 59 percent over current estimated emissions.

Table 1-2 shows the emission reduction possible from chemical plants as a function of cost effectiveness. Emission reductions are broken down by type of emission.

TABLE 1-2. ACHIEVABLE CCl_4 EMISSION REDUCTION AS A FUNCTION OF COST EFFECTIVENESS[a]

Cost Effectiveness Range, $/Mg of VOC	Nationwide CCl_4 Emission Reduction, Mg/Yr				
	Process Vents	Fugitive	Storage Tanks	Loading	Total
Credit	----	----	5.8	----	5.8
0 - 500	229.4	210.3	41.5	----	481.2
500 - 1,000	30.8	240.9	50.3	----	322.0
1,000 - 2,000	136.1	20.1	14.8	----	171.0
2,000 - 5,000	243.4	18.3	12.8	----	274.5
>5,000	155.3	36.0	5.1	58.2	254.6
TOTAL	795.0	526.6	130.3	58.2	1,510.1

[a] Based on emission estimates and other data for all plants responding to EPA information request. This represents all CCl_4 production facilities and other plants accounting for 95 percent of domestic CCl_4 consumption.

2.0 INTRODUCTION

This document identifies the sources and locations of carbon tetrachloride (CCl_4) emissions, estimates total production volumes and emission levels, identifies the applicable control technologies for each emission source, and estimates the costs of controlling emission sources which are presently not well controlled. The information collected in this source assessment study will also be used by the U.S. Environmental Protection Agency (EPA) to refine estimates of human exposure to CCl_4.

2.1 APPROACH

Information for this document was acquired from various sources. The approach to information gathering for each of these sources is discussed in the following paragraphs.

Background information such as previous EPA documents and other published literature was reviewed in an attempt to identify the producers of CCl_4 and the major uses and applications. Six companies producing CCl_4 at ten facilities were identified. Ethylene dichloride (EDC) production was identified as a source of byproduct CCl_4 formation in the literature. A total of twelve companies producing EDC were identified, two of which also produce CCl_4. Nine of these EDC producers and all six companies producing CCl_4 were sent information request under the authority of Section 114 of the Clean Air Act (CAA). These letters requested detailed information on CCl_4 emissions and control techniques for all possible emission sources associated with production and use of CCl_4. Information on the total quantity of CCl_4 produced and sold in 1983 were also requested.

The available literature was also reviewed to identify major uses of carbon tetrachloride. Chlorofluorocarbon 11 and 12 production was identified as the major use accounting for 90 to 95 percent of total use. Five companies producing CFC 11 and 12 at 8 facilities were identified.

Other potentially large users of CCl_4 cited in the literature were chlorine production, phosgene/isocyanate production, production of chlorinated paraffins, Hypalon^R production, and production of pesticides. All identified producers of chlorine, phosgene, and Hypalon^R were contacted to verify the use of CCl_4. Six companies producing chlorine and the single producer of Hypalon^R were verified as users of CCl_4. One producer of chlorinated paraffins was also verified as a user of CCl_4. Of these eight identified users, five had already received the EPA information request since they were also CCl_4 and EDC producers. Information requests were sent to the remaining three identified users and all five producers of CFC 11 and 12 under authority of Section 114 of the CAA. These letters requested detailed information on CCl_4 emissions and control techniques for all sources of emissions associated with the use of CCl_4. A detailed discussion on the types of emission data provided in company responses is presented in Section 2.2. All companies were asked only to estimate emissions. No testing was required to be done specifically for this information request.

Plant trips were taken to Vulcan Chemicals in Geismar, LA, Dow Chemical U.S.A. in Plaquemine, LA, and Stauffer Chemical in LeMoyne, AL to gain familiarity with each of the CCl_4 production processes, emission sources, and emission controls at these facilities. A visit was also made to Kaiser Aluminum and Chemical in Gramercy, LA to gain familiarity with the CFC 11 and 12 production process. Meetings were held with plant representatives to discuss operating procedures, the process equipment used, potential emission sources, and methods of emissions control.

2.2 EMISSION SOURCES

This section presents a brief description of the types of emission information obtained from Section 114 responses and how this information was used to estimate emissions. Emission sources at facilities producing or using CCl_4 can be categorized into process vent, equipment leak, storage, loading/handling, secondary, equipment opening, and relief device discharge emissions.

2.2.1 Process Vent Emissions

Carbon tetrachloride emissions can originate from the purging of inert gases from reactor vessels, drying beds, finishing columns and other process vessels. These emissions may be continuous or intermittent. The process vent data provided by companies in Section 114 responses included the vent steam characteristics before and after the control device (if present), the estimated uncontrolled CCl_4 and VOC emissions (at full capacity), information on the vent stream control device, and the estimated pollutant efficiency of the control device. The estimated process vent emissions presented in this report are based on the company supplied estimates of uncontrolled emissions and control device efficiency unless otherwise noted. All process emission estimates are at full capacity. Process vent emissions may vary directly with capacity utilization of the process.

2.2.2 Equipment Leak Emissions

Equipment leak emissions are considered to be those volatile organic compound (VOC) emissions that result when process fluid (either liquid or gaseous) leaks from plant equipment. Equipment leak emissions were estimated from the following sources: pumps, compressors, process valves, open-ended lines, sampling connections, flanges, and relief valves in gas service. Equipment leak emissions are generally random occurrences which cannot be predicted.

Chemicals transferred by pumps can leak at the point of contact between the moving shaft and stationary casing. Consequently, all seal type pumps require a seal at the point where the shaft penetrates the housing in order to isolate the pump's interior from the atmosphere.

Compressors are similar to pumps in their need for shaft seals to isolate the process gas from the atmosphere. As with pumps, these seals are likely to be the source of emissions.

The most common piece of equipment in a chemical plant is one of the following types of valves: control, globe, plug, ball, diaphram, and check. All except the check valve are activated by a valve stem. The stem requires a seal to isolate the process fluid inside the valve from the atmosphere. The possibility of a leak through this seal makes it a potential source of emissions. Check valves and diaphram valves have no stem or seal and are, therefore, not considered a potential source of equipment leak emissions.

Some valves are installed in a system so that they function with the downstream line open to the atmosphere. Examples are purge valves, drain valves, and vent valves. A faulty valve seat, or an incompletely closed valve would result in leakage of VOC emissions through the valve.

The operation of a process unit is checked periodically by routine analyses of feedstocks and products. To obtain representative samples for these analyses, sampling lines must first be purged prior to sampling. The purged liquid or vapor is sometimes drained onto the ground or into a sewer drain, where it can evaporate and release VOC emissions to the atmosphere.

Flanges are bolted, gasket-sealed junctions used whenever pipe or other equipment may require isolation or removal. The primary cause of flange leakage is due to thermal stress that piping or flanges in some services undergo; this results in the deformation of the seal between the flange faces. Flanges may also become emission sources when leakage occurs due to improperly chosen gaskets or a poorly assembled flange.

Relief valves are typically spring-loaded and designed to open when the process pressure exceeds a set pressure, allowing the release of vapors until the system pressure is reduced. The seal is a disk on a seat, and the possibility of a leak through this seal makes it a potential source of emissions.

The quantity of VOC equipment leak emissions from each of these sources were estimated using VOC emission factors presented in Fugitive Emission Sources of Organic Compounds - Additional Information Document.[1] These factors are presented in Table 2-1. The number of each type of equipment in CCl_4 service was supplied in company responses to the Section 114 letters. Equipment count data provided by the companies was for six ranges of CCl_4 service: less than 5 percent, 5 to 10 percent, 10 to 25 percent, 25 to 75 percent, 75 to 99 percent, and greater than 99percent. The methods used for estimating CCl_4 emissions based on these data are presented in

TABLE 2-1. VOC EMISSION FACTORS FOR EQUIPMENT LEAKS[a]

Equipment Type	VOC Emission Factor kg/d	VOC Emission Factor Mg/yr
1. Pump Seals		
- Packed	1.19	0.43
- Mechanical	1.19	0.43
- Double Mechanical	0.0	0.0
2. Compressors	5.47	2.0
3. Flanges	0.02	0.01
4. Valves		
- Gas	0.13	0.05
- Liquid	0.17	0.06
5. Pressure Relief Device		
- Gas	2.50	0.91
- Liquid	0.0	0.0
6. Sample Connections		
- Gas	0.36	0.13
- Liquid	0.36	0.13
7. Open-Ended Lines		
- Gas	0.04	0.015
- Liquid	0.04	0.015

[a] Reference 1.

Appendix B. Unless a company supplied actual test data, uncontrolled emission factors were used for estimating fugitive emissions. It should be noted that some plants indicated existence of formal leak detection and repair programs for pumps, valves, and flanges. However, the plants either did not report the frequency of repair or the indicated repair frequency was so infrequent (e.g. annual) that EPA's Leak Detection and Repair Model (LDAR) estimates minimal emission reductions.[1] Also, several companies indicated visual inspection programs, but no emission reduction was estimated for these programs. Some companies indicated safety relief valves that are protected by rupture disc or a control device. Emissions were not estimated to be zero for the controlled relief valves.

2.2.3 Storage Emissions

The three types of CCl_4 storage tanks used are:

(1) fixed roof tanks;
(2) internal floating roof tanks; and
(3) pressure vessels.

A typical fixed roof tank consists of a cylindrical steel shell with a dome- or cone-shaped permanently affixed roof. The majority of tanks for storing CCl_4 are fixed roof.

The major types of emissions from fixed-roof tanks are breathing and working losses. Breathing losses are expulsions of vapor from the tank vapor space which expands or contracts because of daily changes in ambient temperatures and barometric pressures. These emissions occur in the absence of any liquid level changes in the tank.

Working losses occur when a tank is filled or emptied. During filling, the tank liquid level rises, increasing internal pressure in the vapor space. To release excess pressure, vapors are vented to the atmosphere. Emptying losses occur when the air drawn into the tank during liquid removal expands as a result of reaching temperature and saturation equilibrium. When this occurs, the fixed capacity of the vapor space is exceeded and the vapors are released through a pressure relief device.

Internal floating roof tanks have both permanently affixed roofs and roofs which float inside the tanks on the liquid surface (contact) or supported by pontoons several inches above the liquid surface (non-contact). The internal floating roof rises and falls with the level of liquid change in the tank. Internal floating roof tanks may be equipped with primary or primary and secondary seals. Primary seals are typically perimeter flexible seals filled with liquid or gas that slide against the tank well. Secondary seals are typically a flexible wiper around the perimeter of the floating roof.

Losses of VOC vapors from under floating roofs occur in one of four ways: through the annual rim space around the perimeter of the floating roof (rim or seal losses), through the openings in the deck required for various types of fittings (fitting losses), through the nonwelded seams formed when joining sections of the deck material (deck seam losses), and through evaporation of liquid left on the tank wall following withdrawal of liquid from the tank (withdrawal loss). There are a number of potential mechanisms for seal losses which are not discussed here. The reader is referred to VOC Emissions from Volatile Organic Liquid Stroage Tanks - Background Information for Proposed Standards for additional discussion of seal, fitting, and seam losses. The seal, fitting, and deck seam losses occur not only during the working operations of the tank, but also during free standing periods. Overall the emissions from internal floating roof tanks are generally less than 4 Mg/yr.

Pressure vessels are designed to store materials at their vapor pressure or at high internal pressures. They are generally used for storing highly volatile and/or toxic materials and are constructed in various sizes and shapes, depending on the operating pressure range. High pressure vessels (up to 1827 kPa) can be operated so that virtually no breathing or working losses occur. Working losses can occur in low pressure (117 to 207 kPa) tanks due to atmospheric venting during filling operations.

Methods presented in the background information document (BID) for Volatile Organic Compound Emissions from VOL storage were used to estimate uncontrolled CCl_4 emissions from fixed roof and internal floating roof storage tanks.[2] These methods are presented in Appendix B. Data on the tank type, size, height, diameter, and throughput for the 1983 calendar year were obtained from Section 114 responses. Emissions from low pressure tanks were estimated using only the working loss portion of methods for estimating fixed roof tank emissions.

2.2.4 Loading/Handling Emissions

Loading emissions occur when loading CCl_4 into tank trucks, rail tank cars, barges, etc.. Carbon tetrachloride emissions occur when vapor in empty cargo spaces is displaced by the CCl_4 liquid being loaded. The displaced vapor contains small to saturation quantities of CCl_4. Handling emissions result during connecting and disconnecting of transfer lines when loading or unloading CCl_4. Residual quantities of liquid or vapor CCl_4 may escape from the line to the atmosphere especially if the lines are not capped after use.

Estimated loading and handling emissions were supplied by companies in Section 114 responses. Most companies provided estimates based on 1983 throughputs. The emission estimates presented in this report were obtained from Section 114 responses unless otherwise noted.

2.2.5 Secondary Emissions

Secondary emissions occur during the treatment and/or disposal of wastewater, liquid wastes or solid wastes on site. Companies provided the estimated CCl_4 rate (kg/day) in waste streams, the disposal or treatment method, and estimated the fraction of CCl_4 emitted to the atmosphere on site in Section 114 responses. Secondary emission estimates presented in this report are based on the reported effluent rate of CCl_4, the estimated fraction going to the atmosphere, and 365 days of operation per year. Publicly owned treatment works (POTWs) are also a source of CCl_4 secondary emissions if CCl_4 process wastes are not treated on-site. Emissions from POTWs are discussed separately in Section 12.1.

2.2.6 Equipment Opening Emissions

Equipment opening emissions occur when process equipment which are closed during operation are opened for maintenance. Liquid and/or vapors remaining in the lines are then released to the atmosphere. In Section 114 responses, companies provided an estimate of the number of equipment openings in 1983 and the resulting emissions.

2.2.7 Relief Device Discharge Emissions

Relief devices are used to exhaust excess pressure built-up during process upset conditions. The most common type device used, relief valves, are spring-loaded and designed to open when the process pressure exceeds a set pressure, allowing the release of vapors or liquids until the system pressure is reduced to its normal operating level. Circumstances leading to overpressure conditions and subsequent relief device discharge are random. Companies supplied the number of relief device discharges which occurred in 1983 and estimated the resulting emissions for each release.

2.3 AVAILABLE CONTROLS FOR EMISSION SOURCES

Emissions from chemical production facilities can currently be controlled in a variety of ways. This section will briefly describe some of the most efficient control methods for each emission category and identify those for which costs were evaluated in this study. All costs presented in this report are in 4th quarter 1984 dollars.

2.3.1 Process Vent Emission Controls

Emissions from process vents can be ducted to a control device such as an incinerator, condenser, or carbon adsorber. Destruction efficiencies of 98 percent or greater are achievable for incinerators. The control efficiency for condensers typically ranges from 50 percent to 95 percent depending on stream concentration and condenser operating temperature. A control efficiency of 95 percent can normally be obtained with carbon adsorbers. The control technique for which costs were evaluated in this study was incineration. It was assumed that all process vent emissions for a single process unit can be ducted to a common incinerator. The costs for incineration were estimated using methods presented in Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry - BID.[3,4] Costs estimates presented in this report for incineration were developed using the new case factors (i.e. not retrofit). It should be noted that these incinerator cost estimates are preliminary. Attempts are being made to obtain updated cost information for small incinerators. The costs of 100 feet of additional duct and pipe rack were included for each additional vent when incineration was evaluated for multiple vents. The cost methods used and a sample calculation are presented in Appendix C.

Also, carbon adsorption control was evaluated for control of process vent emissions at chlorine plants. Costs for this control technique were estimated using techniques presented in Capital and Operating Costs of Selected Air Pollution Control Systems.[5] It should be noted that costs estimates presented in the report are based on costs for steam regeneration units. The carbon adsorber presently used by chloride producers are regenerated by hot nitrogen. No cost information is available for these units, but it is expected that they are more expensive.

2.3.2 Equipment Leak Emission Controls

Equipment leak emissions may be reduced by using process equipment which are designed specifically to prevent leakage or by implementing a leak detection and repair program. The control that can be achieved by equipment leak control techniques is presented in Table 2-2 and discussed in the following paragraphs.

Pumps and compressors leak at the interface of a moving shaft and a stationary casing. Equipment specifications that may be implemented for pumps include elimination of this junction, improvement of the seal at the junction, or collection and control of the emissions from the junction.

Emissions from open-ended lines can be controlled by installing a cap, plug, flange, or second valve to the open end of the valve. The control efficiency will be dependent on the frequency of removal of the cap or plug.

TABLE 2-2. CONTROL TECHNIQUES FOR CONTROLLING EQUIPMENT LEAKS[a]

Equipment Type (Emission Source)	Control Techniques	Percent Reduction
1. Pump Seals		
- Packed	Monthly LDAR	61
- Mechanical	Monthly LDAR	61
- Double Mechanical	N/A	N/A
2. Compressors	Vent to Combustion Device	100
3. Flanges	None Available	N/A
4. Valves		
- Gas	Monthly LDAR	73
- Liquid	Monthly LDAR	59
5. Pressure Relief Devices		
- Gas	O-Ring	100
- Liquid	N/A	N/A
6. Sample Connections		
- Gas	Closed-Purge Sampling Systems	100
- Liquid	Closed-Purge Sampling Systems	100
7. Open-Ended Lines		
- Gas	Caps on Open Ends	100
- Liquid	Caps on Open Ends	100

LDAR - Leak detection and repair.
N/A - Not applicable.

[a] Reference 6.

Caps, plugs, etc. for open-ended valves do not affect emissions which may occur during use of the valve. These emissions may be caused by line purging for sampling, draining, or venting through the open-ended valve.

Equipment leak emissions from sampling connections can be reduced by using a closed loop sampling system. The closed loop system is designed so that the purged fluid is returned to the process at a point of lower pressure. Closed loop sampling is assumed to be 100 percent effective for controlling emissions from sample connections.

Emissions from valves occur at the stem or gland area of the valve body. Diaphragm and bellows seal valves do not have a stem or gland and, therefore, are not prone to equipment leak emissions. Their control effectiveness is approximately 100 percent, although a failure of the diaphragm or bellows may cause large temporary emissions. The applicability of these valves is only limited because of process conditions or cost considerations.

The use of portable instrument monitors for the detection of leaks allows plant personnel to inspect individual components. There are several factors which determine the control efficiencies of individual component surveys; these include:

- Action level or leak definition,
- Inspection interval or monitoring frequency,
- Achievable emission reduction of maintenance, and
- Interval between detection and repair of the leak.

Estimates of control efficiencies for such programs vary because of the factors mentioned above. Controls specified by the benzene equipment leak emissions NESHAP were evaluated for control of CCl_4 equipment leaks.[6] Those control techniques are listed in Table 2-2. The costs of these techniques are discussed in the following sections and cost estimating methods are presented in Appendix C.

2.3.3 Storage Emission Controls

Emissions from uncontrolled fixed roof tanks can be reduced through the use of add-on controls or by equipping the tank with an internal floating roof. The add-on controls are actually separate from the tank. Emissions from the tank are ducted to the control device. These devices include thermal oxidation units (incinerators) and various types of refrigeration systems. The efficiency of incinerators is reported to be greater than 98 percent, while greater than 85 percent efficiency can generally be obtained by a refrigeration system.

Depending on the type of roof, seal system selected, and the tank operating parameters, an internal floating roof will reduce fixed roof tank emissions by as much as 97 percent. Floating roofs are technically limited to tanks greater than 2 meters in diameter and are not applicable to horizontal tanks.

Refrigerated vent condensers are add-on devices which may be used on low pressure tanks for control of working loss emissions. Condensers are, however, generally less cost effective than floating roofs. Three options were evaluated in this study for control of storage emissions from fixed roof tanks. They are a contact internal floating roof with primary seal only, a contact internal floating roof with primary and secondary seals, and a refrigerated vent condenser. The control efficiency of a vent condenser was assumed to be 85 percent. Control efficiency of floating roofs were estimated using storage tank data supplied by companies and emission estimating techniques presented in Appendix B. The costs estimates for installation of floating roofs were developed using methods in the Source Assessment Document of Ethylene Dichloride Emissions[7] and tank sizes supplied in Section 114 responses. Costs of a refrigerated condenser were estimated using methods in Cost of Selected Air Pollution Control Systems.[5] These methods are presented in Appendix C.

2.3.4 Loading/Handling Emission Controls

Loading emissions can be reduced by using submerged loading techniques, vapor recovery systems, incineration, vapor balance systems, and carbon adsorption. A brief description of each follows:

Submerged loading is the introduction of a liquid into a vessel with the transfer line outlet below the liquid surface. Submerged loading minimizes droplet entrainment, evaporation, and turbulence. Emission reductions range from 0 to 65 percent.

The vapor balance system consists of a pipeline between the vapor spaces of the receiving vehicle and the unloading storage tank, which essentially creates a closed system. This allows the vapor spaces of the storage tank and the vehicle to balance with each other. The vapor balance system cannot be utilized with floating roof storage tanks.

Vapor recovery systems recover VOC vapors displaced during loading operations by use of refrigeration (e.g., vent condensers). Control efficiencies can range from 90 to 98 percent, depending on the nature of the emissions and the type of recovery equipment used. The vapor adsorption process consists of passing solvent-laden air through a carbon bed. As the air passes through the carbon, the solvent is adsorbed and clean air is exhausted via a valve. With a carbon adsorption system, it is possible to recover the adsorbed solvent for reuse. Efficiencies are generally greater than 95 percent.

Venting emissions to an incinerator can provide 97 to 99 percent emission control. This is the control technique evaluated for control of loading emissions in this report. Handling emissions reported by companies were generally small and control of handling emissions was not evaluated. The costs of incineration for control of packing emissions were estimated using the same methods used for control of process vents. Only vent stream characteristics were not supplied in Section 114 responses. The vent flow was estimated to be equivalent to the approximate liquid loading rate for the vessel being loaded. It was assumed that a common incinerator can be used for all land based loading operations and a common incinerator can be used for all marine loading operations. Vessel loading rates were estimated to be 1,800 gallons per minute (gpm) for ships, 800 gpm for barges, 200 gpm for tank truck and rail cars, and 50 gpm for drums.

2.3.5 Secondary Emission Controls

The best way to control CCl_4 secondary emissions is by reducing the amount of CCl_4 in the waste stream to be treated. Reducing CCl_4 content in the waste stream may be accomplished by steam stripping, carbon adsorption, or better housekeeping at the production facility. Control costs estimates for secondary emissions were not developed in this study.

2.3.6 Equipment Opening Emission Controls

Equipment opening emissions occur only during maintenance operations. These emissions can be easily controlled by purging and collecting the gases or liquids for further treatment before opening the equipment. The emissions may then be treated by incineration, adsorption, condensation, etc. Reported emissions from this source were generally small and no control cost estimates were developed.

2.3.7 Relief Device Discharge Controls

No costs estimates were developed for control of relief device discharge emissions in this study. Control of these emissions will be evaluated in future work.

2.4 REFERENCES

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2. U.S. Environmental Protection Agency. VOC Emissions from Volatile Organic Liquid Storage Tanks - Background Information for Proposed Standards (Draft). Research Triangle Park, North Carolina. Publication No. EPA-450/3-81-003a. July 1984. pp. 4-1 through 4-20.

3. U.S. Environmental Protection Agency. Process in Synthetic Organic Chemical Manufacturing Industry - Background Information Document. Research Triangle Park, North Carolina. Publication No. EPA-450/3-82-001a. January 1982. Appendix E.

4. Memo from Pandullo, R. F. and I. M. McKenzie, Radian Corporation, to Air Oxidation Processes and Distillation Operations Project Files. May 1, 1985. 20p. Revision to the Incinerator Costing Procedures Used for the Proposed Air Oxidation and Distillation NSPS.

5. Neveril, R. B. (GARD, Inc.) Capital and Operating Costs of Selected Air Pollution Control Systems. (Prepared for the U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. Publication No. EPA-450/5-80-002. December 1978. pp. 5-39 through 5-49 and 5-65 through 5-71.

6. U.S. Environmental Protection Agency. Benzene Fugitive Emissions - Background Information Document. Research Triangle Park, North Carolina. Publication No. EPA-450/3-80-032b. June 1982. Appendix A.

7. Atkinson, R. D. (MRI) et al. Source Assessment of Ethylene Dichloride Emissions. (Prepared for the U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. EPA Contract No. 68-02-3817. September 1984.

3.0 CARBON TETRACHLORIDE PRODUCTION

Three production processes are currently used for the production of carbon tetrachloride (CCl_4). They are the hydrocarbon chlorinolysis, hydrochlorination/direct chlorination, and carbon disulfide processes. At present, there are 9 facilities producing CCl_4. The production capacity and process types for these facilities are presented in Table 3-1. The total estimated production capacity of these facilities is about 455,000 Mg/yr. In 1983, total production for these facilities was 278,700 Mg for an overall industry capacity utilization of 61 percent.

The overall capacity utilization for CCl_4 is expected to approach 100 percent in 1985.[1] Following a 19 percent increase in CCl_4 production from 1984 to 1985, DuPont has plans to convert its CCl_4 production facility in Corpus Christi, Texas, to produce chloroform in late 1985.[1] This conversion will shift DuPont from being a 136,000 Mg/yr supplier to a net 68,000 Mg/yr consumer.[1] Also Dow ceased production of CCl_4 by the hydrocarbon chlorinalysis process in June 1985.[2] Producers are projecting a further 5 percent expansion in CCl_4 use in 1985.[1] The increased demands and reduction in capacity will be partially offset by Stauffer's planned expansion in mid-1985. Stauffer plans to expand production at its LeMoyne, Alabama facility by 31,700 Mg/yr.[3] The elimination of grain fumigant use (2.6 percent of 1983 use) should reduce CCl_4 demand slightly.

3.1 CARBON TETRACHLORIDE USES

One of the objectives of this study was to determine if any large unidentified uses of CCl_4 exist. In order to achieve this objective, information was obtained from CCl_4 producers on the amounts of CCl_4 sold to various users in 1983 and the nature of the end use, if known. The CCl_4 producers also provided information on the amounts and nature of any CCl_4 used captively in 1983. Captive use information, along with the inventory

TABLE 3-1. CARBON TETRACHLORIDE PRODUCTION CAPACITIES (1984)[4]

Company	Location	Process	Capacity (Mg/Yr)
Diamond Shamrock	Belle, WV	Hydrochlorination/ Direct Chlorination	2,000
Dow Chemical	Freeport, TX	Hydrocarbon Chlorinolysis[a]	61,200
	Pittsburg, CA	Hydrocarbon Chlorinolysis[a]	36,000
	Plaquemine, LA	Hydrocarbon Chlorinolysis[a]	56,700
E.I. duPont[b]	Corpus Christi, TX	Hydrocarbon Chlorinolysis	136,000
LCP Chemical & Plastics	Moundsville, WV	Hydrochlorination/ Direct Chlorination	4,000
Stauffer Chemical[c]	LeMoyne, AL	Carbon Disulfide	91,000
Vulcan Materials	Geismar, LA	Hydrocarbon Chlorinolysis[a]	41,000
	Wichita, KS	Hydrocarbon Chlorinolysis[a]	27,000
TOTAL			455,000

[a] Crude CCl_4 formed in hydrochlorination/direct chlorination process fed to hydrocarbon chlorinolysis process.

[b] DuPont plans to convert this facility to primarily chloroform and methylene chloride product in late 1985.

[c] Stauffer plans to increase CCl_4 production capacity by 31,700 Mg in mid-1985.

N/A - Not available.

change data (supplied by companies), and the 1983 sales information, was used to estimate 1983 production volume for each company. In addition, information on the amounts of CCl_4 purchased from each producer in 1983 was requested from identified users of CCl_4. This information was used to verify the amounts reported by the producers. In some cases, there were slight discrepancies between the amounts reported by the producers and the users. In general, users reported purchasing somewhat higher amounts of CCl_4 than the producers reported selling to them. The reason for these small discrepancies is not known. Possible explanations are rounding off errors or incomplete records. Also, end of the year shipments in 1982 may have been received in 1983 by the users.

Using the responses provided by the producers and users of CCl_4, material balance calculations were performed. The producers reported total U.S. sales of 258,096 Mg in 1983. An additional 10,505 Mg were exported while 10,934 Mg were used captively by the producers. The users of CCl_4 responding to EPA's information requests reported total purchases of 258,383 Mg from the U.S. CCl_4 producers. This compares with 253,858 Mg that the producers reported selling to these users (EPA did not send information requests to all users). Since the sales volume information provided by the CCl_4 producers was only for domestically produced CCl_4, it is possible that some of the difference between the two amounts is due to CCl_4 imported into the United States from abroad by the domestic producers for resale in the U.S. The International Trade Commission's estimate for 1983 CCl_4 imports is 3,200 Mg[4]. No information was obtained in this study about the distribution channels for imported CCl_4.

The sales, captive use, and inventory change information provided by CCl_4 producers was used to estimate 1983 production of CCl_4 in the United States. It is estimated that 275,350 Mg of CCl_4 were produced in 1983. It should be noted that one producer did not provide data on inventory change. It was assumed that for this producer CCl_4 inventory did not change in 1983. This may explain at least some of the difference between the production estimates presented in this study and the 259,430 Mg reported by the U.S. Department of Commerce[4].

Figure 3-1 presents estimates for CCl_4 production, sales, and the amounts used in various applications. This information is based on the data provided by the producers (discrepancies with the amounts reported by the users were ignored). As can be seen from the figure, there are no large unidentified uses of CCl_4.

In this study, plant specific emission information was obtained for about 95 percent of the 1983 CCl_4 use (captive and sales). An additional 2.7 percent of the use was in grain fumigants. All CCl_4 used in grain fumigants is expected to be emitted to the atmosphere. No specific emission information was obtained in this study on the remaining 2.3 percent (6,060 Mg) of CCl_4 use. These uses include miscellaneous chemical processes, pesticide production, and other miscellaneous uses. The companies and locations were identified for 5,400 Mg of the remaining use in this study. Emissions information for these uses will be obtained in future work. Only the end uses of CCl_4 sold through distributors (660 Mg) are left unidentified.

3.2 HYDROCARBON CHLORINOLYSIS PROCESS

There are currently six facilities producing CCl_4 by the hydrocarbon chlorinolysis process. As presented in Table 3-1, this process accounts for approximately 80 percent of CCl_4 production capacity. This is often called the perc/tet process since perchloroethylene (PCE) is formed as a co-product.

3.2.1 Process Description

A variety of feedstocks are used in the production of CCl_4 by the hydrocarbon chlorinolysis process including propane, propylene, acetylene, napthalene, ethylene dichloride, and crude CCl_4 from the hydrochlorination/direct chlorination process. A process flow diagram is presented in Figure 3-2. Fresh chlorine along with recycled chlorine, and hydrocarbon feed are introduced into a vaporizer where they are mixed with recycled chlorides. The mixed gases at atmospheric pressure, are fed to a refractory lined reactor. The reactor operates at high temperatures, typically between 550°C and 700°C. A reaction similar to the following takes place depending on the feed:

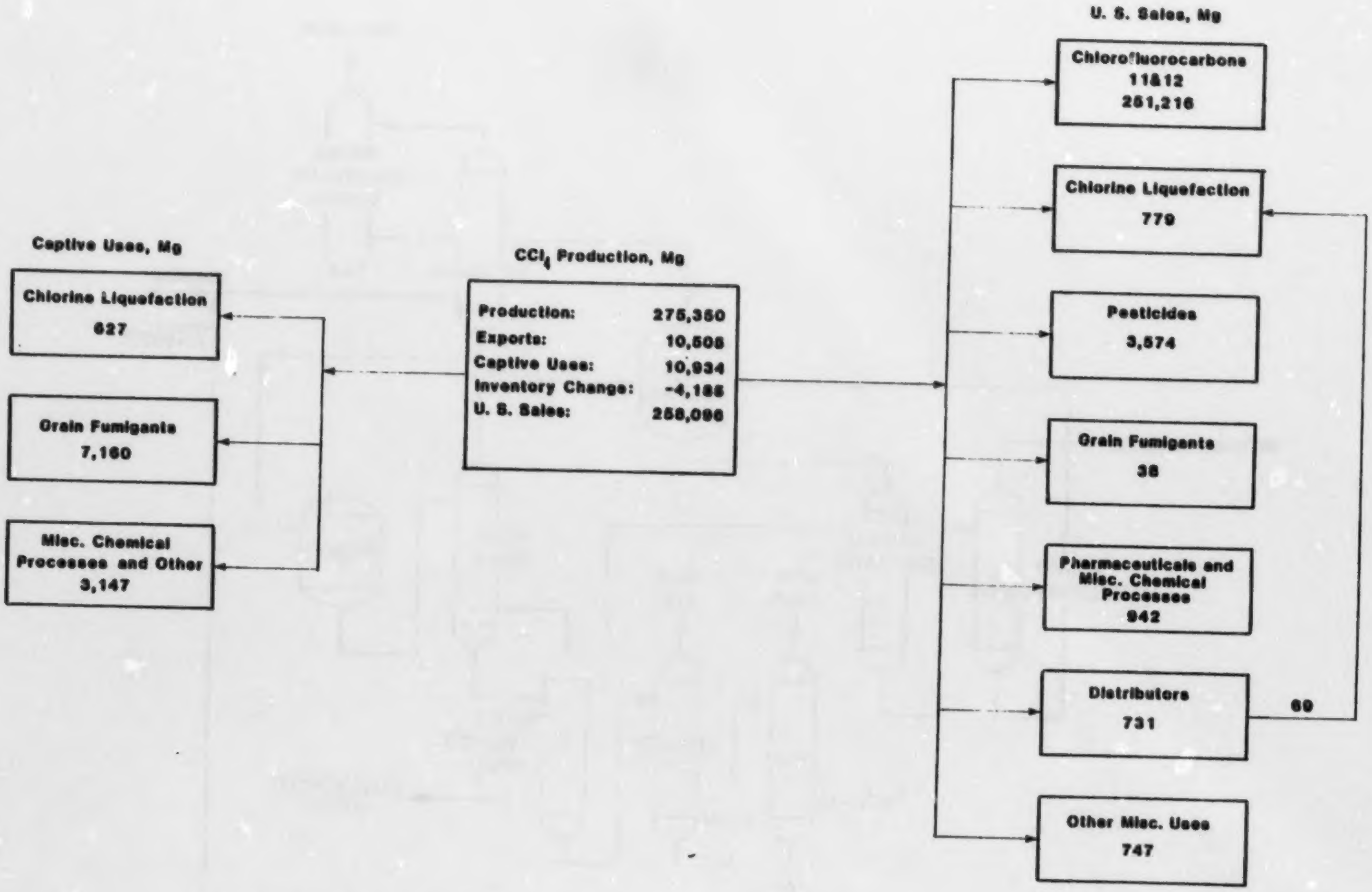
Captive Uses, Mg
Chlorine Liquefaction
627
Grain Fumigants
7,160
Misc. Chemical Processes and Other
3,147
CCl4 Production, Mg
Production: 275,350
Exports: 10,506
Captive Uses: 10,934
Inventory Change: -4,186
U. S. Sales: 258,096
U. S. Sales, Mg
Chlorofluorocarbons 11&12
251,216
Chlorine Liquefaction
779
Pesticides
3,574
Grain Fumigants
38
Pharmaceuticals and Misc. Chemical Processes
942
Distributors
731
60
Other Misc. Uses
747

Figure 3-1. 1983 Production, Sales, and Use Estimates for CCl_4.

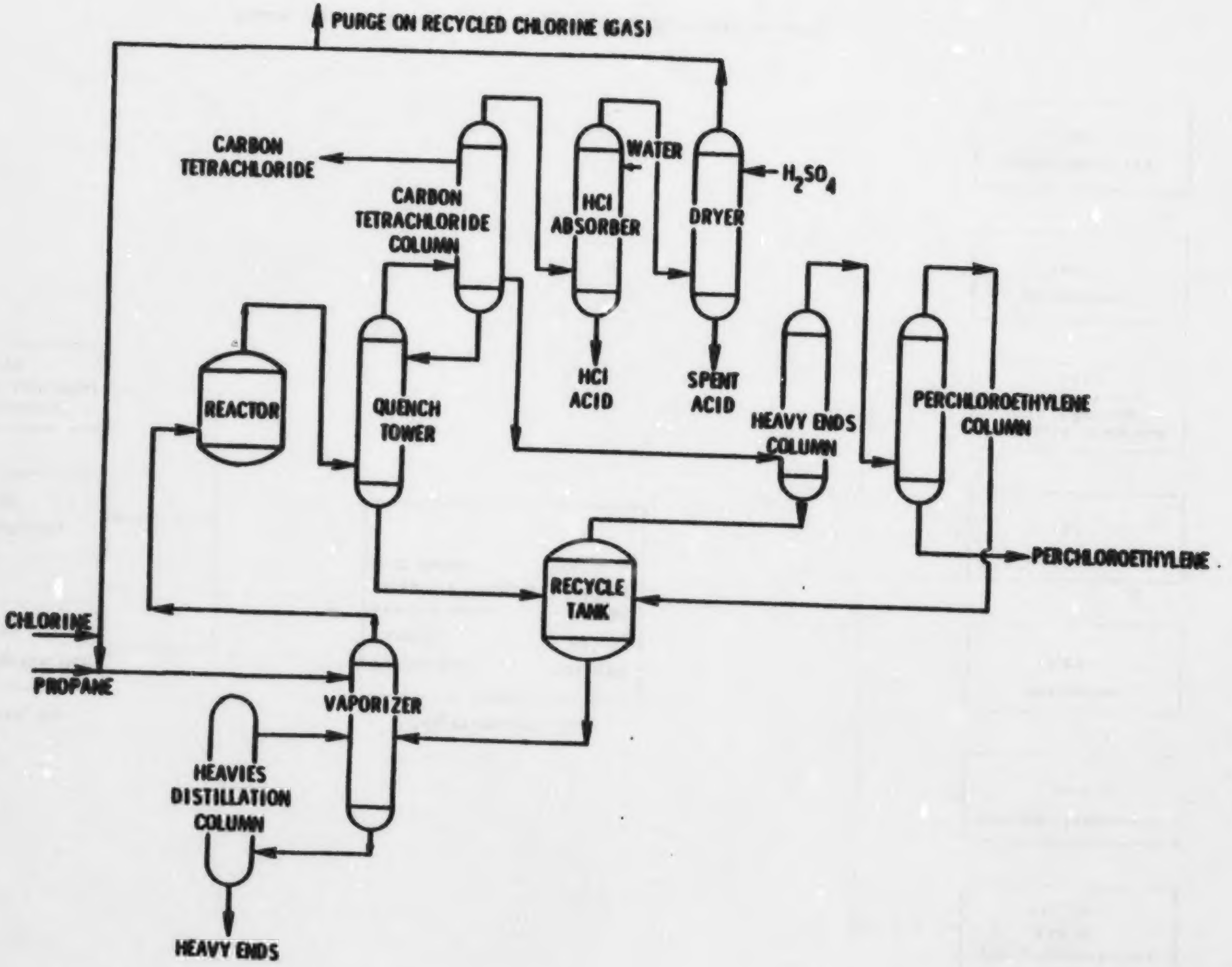
PURGE ON RECYCLED CHLORINE (GAS)
CARBON TETRACHLORIDE
CARBON TETRACHLORIDE COLUMN
HCl ABSORBER
WATER
DRYER
H_2SO_4
HCl ACID
SPENT ACID
REACTOR
QUENCH TOWER
HEAVY ENDS COLUMN
PERCHLOROETHYLENE COLUMN
PERCHLOROETHYLENE
RECYCLE TANK
CHLORINE
PROPANE
VAPORIZER
HEAVIES DISTILLATION COLUMN
HEAVY ENDS

Figure 3-2. Carbon tetrachloride by the hyrocarbon chlorinolysis process.

$$C_3H_8 + 8Cl_2 \xrightarrow{550 \text{ to } 700^\circ C} CCl_4 + C_2Cl_4 + 8HCl$$

(propane) (chlorine) (carbon tetrachloride) (perchloroethylene) (hydrogen chloride)

After startup, the reaction is self-sustaining. The diluent action of recycled chlorides is used to control the CCl_4/PCE ratio.[5]

Effluent from the reactor consists mainly of CCl_4, PCE, hydrogen chloride, and excess chlorine along with unreacted hydrocarbons. The hot effluent gas is quenched, followed by removal of HCl and Cl_2. The liquid stream from the quench is separated into product CCl_4 and PCE by distillation. Heavy ends are recycled back to the feed tank.

3.2.2 Current Controls and Emissions

The primary types of emissions from this process are process vent, fugitive (equipment leaks), storage, and loading emissions. In addition, relatively small emissions occur from equipment openings (usually for maintenance), emergency relief device discharges, and secondary emissions from waste stream handling and treatment. A summary of estimated emissions by facility and type is presented in Table 3-2. Total emissions from all facilities using the hydrocarbon chlorinolysis process is estimated to be 513 Mg/yr.

The estimated emissions for each facility along with present controls are presented in Table 3-3 by individual emission source. All emission estimates presented in Table 3-3 were obtained directly from company response to a Section 114 request except equipment leak and storage emissions which were estimated using EPA estimating methods and company supplied data. Methods used for estimating equipment leak and storage emissions are presented in Appendix B.

As shown in Tables 3-2 and 3-3, total estimated emissions at individual facilities range from 29.8 Mg/yr at the Dow/Pittsburg facility to 113 Mg/yr at the Vulcan/Wichita facility. The significantly lower estimated emissions for the Dow/Pittsburg facility are mainly attributed to the low reported equipment leak emissions at this facility. Dow supplied test results from a

TABLE 3-2. SUMMARY OF 1983 ESTIMATED CCl_4 EMISSIONS FROM CARBON TETRACHLORIDE PRODUCTION FACILITIES (Mg)

Company/Location	Process	Equipment Leak	Storage	Loading	Relief Device	Equipment Op.	Secondary	Total
HYDROCARBON CHLORINOLYSIS PROCESS								
E.I. DuPont/Corpus Christi, TX	16.3	60.0	8.85	4.54	1.9	1.6	2.2	95.4
Dow/Freeport, TX	29.5	67.0	4.10	3.14	-	0.18	0.17	104.1
Dow/Plaquemine, LA	9.0	68.0	2.16	17.0	0.19	2.67	1.53	100.6
Dow/Pittsburg, CA	0	0.56	21.3	6.3	<0.01	1.6	0.87	29.8
Vulcan/Geismar, LA	6.54	53.4	9.0	1.0	-	0.07	0.19	70.2
Vulcan/Wichita, KS	0.36	92.6[a]	16.2	0.7	-	3.4	-	113.2
SUBTOTAL	61.7	341.6	61.6	32.7	2.1	9.5	4.1	513.3
HYDROCHLORINATION/DIRECT CHLORINATION PROCESS								
LCP Chemicals/Moundsville, WV	11.8	14.3	1.2	1.9	-	-	0.3	29.5
Diamond Shamrock/Belle, WV	0.24	26.2	0.52	0.1	0.05	0.05	1.5	28.7
Dow/Freeport, TX	<0.001	5.73	0.02	-	-	0.01	0.03	5.8
Dow/Plaquemine, LA	0.2	3.9	0.98	-	-	0.05	-	5.1
Vulcan/Geismar, LA	0.7	8.18	-	-	-	-	-	8.9
Vulcan/Wichita, KS	0.7	-[a]	-	-	-	-	-	0.7
SUBTOTAL	13.6	58.4	2.72	2.0	0.05	0.11	1.8	78.7
CARBON DISULFIDE PROCESS								
Stauffer/LeMoyne, AL	138.9	74.2	66.5	25.8	-	0.04	0.2	305.6
TOTAL	214.2	474.2	130.8	60.5	2.2	9.5	6.1	897.6

[a] Combined equipment counts for hydrocarbon chlorinolysis and hydrochlorination/direct chlorination process were repeated by Vulcan in Section 114 response. Total estimated emissions for both processes are presented under hydrocarbon chlorinolysis process.

TABLE 3-3. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT FACILITIES PRODUCING CARBON TETRACHLORIDE BY THE HYDROCARBON CHLORINOLYSIS PROCESS

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl$_4$ Emissions (Mg/Yr)	Comments
E.I. duPont/ Corpus Christi, TX[6]	Process Vents				
	- Chlorocarbons Sniff Scrubber	None	0	16.3	Continuous vent from 6 sources
	- Pressure Relief Device Discharge	None	0	1.9	19 discharges
	Equipment Leak	None	0	60.0	
	Equipment Openings	None	0	1.6	2 openings
	Storage				
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.9	974,000 gallon tanks with mechanical shoe, primary seal only.
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.9	
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.9	
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.0	76,000 gallon tanks with vapor filled, primary seal only.
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.0	
	- Contact Internal Floating Roof	Conservation Vent	N/A	1.0	
	- Fixed-Roof Tank	None	0	.15	5,000 gallons
	Handling				
	- Tank Cars	Refrigerated Condenser	86	0.45	
	- Ships	None	0	0.09	
	- Barges	None	0	4.0	
	Secondary				
	- Organic/H$_2$O from Sumps	Deep Well Injection	100	0	
	- Filter Cartridge	Land Fill	100	0	
	- Contaminated Oil	Land Fill	100	0	
	- Tank Sludge	Land Fill	100	0	
	- Dry Column Decante Overflow	None	0	2.2	
	TOTAL			99.0	
Dow Chemical/ Freeport, TX[7]	Process Vents				
	- CCl$_4$ Check Tank	*	*	0.62	
	- Feed Tank	*	*	28.90	
	Equipment Leak	None	0	67.0	
	Equipment Openings	None	0	0.18	200 openings
	Storage				
	- Fixed-Roof Tank	Refrigerated Condenser	95	0.06	49,000 gallon
	- Fixed-Roof Tank	Refrigerated Condenser	95	0.06	49,000 gallon
	- Fixed-Roof Tank	Refrigerated Condenser	95	0.80	1,060,000 gallon
	- Fixed-Roof Tank	Refrigerated Condenser	95	0.80	1,060,000 gallon
	- *	*	*	2.0	
	- *	*	*	0.38	

TABLE 3-3. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Dow Chemical/ Freeport (Cont.)	Handling				
	- Ships, Barges, Rail Cars, Tank, Truck, and Drums	None	0	3.14[a]	
	Secondary				
	- Wastewater Stream #72	Permitted Wastewater	0	0.17	
				104.1	
Dow Chemical/ Plaquemine, LA[a]	Process Vents				
	- Exchanger C-2 Vent	None	0	8.13	
	- Scrubber C-8	None	0	.87	Intermittent, 12 days/yr for 24 hours
	- Thermal Oxidizer	N/A	N/A	<.01	Emissions from oxidizing CCl_4 liquid
	Pressure Relief Discharge	None	0	.19	1 release
	Equipment Leak	None	0	68.0	
	Equipment Openings	None	0	2.67	
	Storage				
	- Fixed-Roof Tank	Thermal Oxidizer	98[b]	<0.01	241,200 gallon
	- Fixed-Roof Tank	Refrigerated Condenser	90	0.04	12,600 gallon
	- Fixed-Roof Tank	Refrigerated Condenser	90	2.12	434,700 gallon
	Handling				
	- Barge, Rail Car, and Tank Truck	Submerged Fill	N/R	17.0	
	Secondary				
	- Containment & Storm Water	Stream Strip/Organics	50	0.05	
	- Water Outfall 005A	Incinerated	N/A	1.44	Emissions from handling
	- Water Outfall 005B	None	N/A	0.04	
	- Filter Media Solid Waste	Incinerator	N/R	<0.01	
	TOTAL			100.6	

TABLE 3-3. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Dow Chemical/ Pittsburg, CA[9]	Process Vents				
	- Reflux Drum Vent	*	*	0	Vents upon startup or change in reflux temp.
	Pressure Relief Device	None	0	<0.01	2 releases
	Equipment Leak	Annual LDAR + Fixed Point Monitors	N/R	0.56[c]	
	Equipment Opening	None	0	1.6	300 openings
	Storage				
	- Pressure Tank	Vapor Return	100	0	25,000 gallon
	- Pressure Tank	Vapor Return	100	0	25,000 gallon
	- Fixed Roof Tank	None	0	2.6	17,000 gallon
	- Fixed Roof Tank	None	0	2.6	17,000 gallon
	- Fixed Roof Tank	Back Pressure Regulator	Slight	16.1	700,000 gallon
	Handling				
	- Rail Cars, Tank Trucks,	None	0	6.3	
	TOTAL			29.8	
Vulcan Materials/ Geismar, LA[10]	Process Vents				
	- CCl_4 Tower	N_2 Pad	N/R	0.79	
	- D-245 Solvent Storage Tank	N_2 Pad	N/R	1.15	
	- D-223A Solvent Check Tank	Glycol Pot	N/R	1.15	Each tank vents 25% of the time
	- D-223B Solvent Check Tank	Glycol Pot	N/R	1.15	
	- D-223C Solvent Check Tank	Glycol Pot	N/R	1.15	
	- D-223D Solvent Check Tank	Glycol Pot	N/R	1.15	
	Equipment Leak	None	0	53.4	
	Equipment Opening	None	0	0.07	
	Storage				
	- Fixed-Roof Tank	*	*	3.2	
	- Fixed-Roof Tank	*	*	5.8	
	Handling				
	- *	*	*	1.0	
	Secondary				
	* *	*	*	0.19	
	TOTAL			70.2	

TABLE 3-3. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Vulcan Materials/ Wichita, KS[11]	Process Vents				
	- D-109 Reflux Drum	None	0	0.36	Intermittent, vented 10 times/yr for 2 hours
	Equipment Leak	None	0	92.6	
	Equipment Opening	None	0	3.4	119 openings
	Storage				
	- Fixed-Roof Tank	Glycol Seal	N/R	0.81	7,500 gallon
	- Fixed-Roof Tank	Glycol Seal	N/R	0.81	7,500 gallon
	- Fixed-Roof Tank	Glycol Seal	N/R	0.79	5,800 gallon
	- Fixed-Roof Tank	Glycol Seal	N/R	0.79	5,800 gallon
	- Fixed-Roof Tank	None	0	0.83	42,000 gallon, 50% CCl_4
	- Fixed-Roof Tank	None	0	0.02	14,600 gallon, 10% CCl_4
	- Fixed-Roof Tank	None	0	0.24	5,800 gallon
	- Fixed-Roof Tank	None	0	11.9	475,000 gallon
	- Pressure Tank	N/A	N/R	No Vent	13,000 gallon
	- Pressure Tank	N/A	N/R	No Vent	6,200 gallon
	Handling				
	- Rail Cars, Tank Trucks, and Drums	None	0	0.7	
	Secondary				
	- N/R	Vapors from Waste Streams Scrubbed	N/R	N/R	
	TOTAL			113.2	

[a] Emission estimated using AP-42.

[b] Company reported greater than 98 perent control, but only 98 percent is accepted without supporting test data.

[c] Dow supplied fugitive test data for this facility supporting this estimate.

N/A = Not Applicable
N/R = Not Reported
* = Confidential Information

study by Science Applications Inc. for the California Air Resources Board (CARB) indicating equipment leak emissions 99 percent lower than those estimated using methods presented in Appendix B. The Dow facility in Pittsburg, California, was the only facility that supplied equipment leak emissions test data. Also, Vulcan/Wichita, the plant with the highest estimated equipment leak emissions supplied equipment count data for the hydrocarbon chloinolysis and hydrochlorination/direct chlorination processes combined. Estimated equipment leak emissions in Tables 3-2 and 3-3 represent the combined equipment leak emissions.

All but one facility, Dow/Pittsburg, reported process vent emissions. Dow did indicate that an unspecified quantity of CCl_4 is emitted at this facility from one process vent upon startup or change in reflux temperature. The total process vent emissions for all facilities are estimated to be 61.7 Mg/yr at full capacity accounting for 12 percent of total emissions from the hydrocarbon chlorinolysis process. Only one facility, Dow/Freeport, presently controls process vent emissions.

Four of the six facilities producing CCl_4 by the hydrocarbon chlorinolysis process are located in either Louisiana or Texas. Both States have regulations requiring control of process vent emissions by combustion or an approved equivalent technology.[12,13] All facilities located in Texas, except Dow/Freeport, are exempt because vent emissions are below the cutoff of 100 lbs/24 hrs. There is no such exemption in Louisiana; however, the control requirements can be waived if the stream is less than 100 tons/yr, will not support combustion without auxiliary fuel, or cause economic hardship. Since all of the process vent emissions are less than 100 tons/yr and will not support combustion, it is most likely that CCl_4 producers in Louisiana have obtained waivers.

Equipment leak emissions account for the majority of the estimated emissions. About 66 percent or 341.6 Mg/yr of the estimated CCl_4 emissions from facilities using the hydrocarbon chlorinolysis process are from equipment leak sources. Although most facilities responded that operators are instructed to perform regular visual inspections for leaks, only one facility, Dow/Pittsburg, California, indicated a formal leak detection and repair program. At this facility annual leak detection and repair is performed and fixed point monitors are used to aid in leak detection. This plant is affected by a Bay Area District regulation requiring repair of leaks greater than 10,000 ppm VOC (at 1 cm) within 15 days for accessible nonessential valves and flanges.[14] For essential valves and flanges, leaks must be minimized within 15 days and repaired within 6 months. The first inspection was required prior to January 1, 1984, and subsequent inspections are required at least annually. Valves and flanges that are identified as leaking must be inspected quarterly.

Louisiana has recently enacted similar regulations; however, the final compliance date is not until December 31, 1987. Two facilities are located in Louisiana which will be affected by this regulation. Requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and valves in liquid service, monthly leak detection for compressor seals and valves in gas service, and weekly visual inspection of pump seals. Repair or reasonable measures to minimize identified leaks is required within 15 days. Also, open ended lines are required to be capped.

Storage tanks are the second largest emission source for facilities producing CCl_4 by the hydrocarbon chlorinolysis process. Storage emissions account for about 61.6 Mg or 12 percent of total annual emissions. As presented in Table 3-3, five of six facilities presently control storage emissions from at least one tank. These five facilities are located in Texas, California (Bay Area District) or Louisiana and are subject to control requirements. All three require control of storage tanks greater than 40,0000 gallons by using pressure tanks, an internal floating roof with primary seal, an external floating roof with primary and secondary seals, refrigerated condenser or combustion technique.[12,13,14] Each of the above-mentioned control techniques, except an external floating roof is presently used by at least one of the five facilities. Refrigerated condensers are used at Dow/Freeport and Dow/Plaquemine with reported efficiencies of 95 and 90 percent, respectively. Thermal oxidation with a reported control efficiency of greater than 98 percent is used for control of one storage tank at Dow/Plaquemine. Contact internal floating roofs are presently used by DuPont in

Corpus Christi, Texas. Pressure tanks with vapor return are presently used at Dow in Pittsburg, California, for control of two 25,000 gallon tanks. It should be noted that both of these pressure tanks are below the 40,000 gallon cutoff exempting them from regulatory requirements. However, one storage tank at the Dow/Pittsburg facility is above the 40,000 gallon cutoff and remains uncontrolled. All other facilities are presently meeting State and local requirements for control of storage tank emissions.

Loading emissions at facilities producing CCl_4 by the hydrocarbon chlorinolysis process account for about 33 Mg or 6 percent of annual emissions from this process. One facility, DuPont/Corpus Christi, controls tank car loading emissions by 86 percent with a refrigerated condenser system. Also, Vulcan in Geismar, Louisiana, controls loading emissions. However, all details on the control system are considered confidential and cannot be discussed. Dow/Plaquemine reported control of loading emissions by submerged fill. The other facilities did not indicate any loading emission controls in their responses.

Four facilities, located in Texas and Louisiana, could be affected by State regulations requiring control of loading emissions. Louisiana requires vapor collection and control for existing VOC loading facilities with greater than 40,000 gallons per day throughput or new facilities with greater than 20,000 gallons per day throughput.[13] Based on estimated CCl_4 production capacity, neither of the facilities located in Louisiana average more than 40,000 gallons per day throughput. But they may still be affected if loading facilities are also used for other VOC products. At facilities in Texas, vapor recovery is required for facilities loading VOC with greater than 20,000 gallons per day throughput.[12] Both facilities located in Texas are estimated to have sufficient production capacity to exceed this cutoff.

Other sources of emissions are pressure relief device discharges (i.e., safety relief valves and rupture discs), opening of equipment for maintenance, and secondary emissions from handling and treatment of waste streams. These emission sources account for about 3 percent (16 Mg) of total annual emissions. There are no applicable State regulations governing these emission sources.

3.3 HYDROCHLORINATION/DIRECT CHLORINATION PROCESS

There are currently six facilities producing CCl_4 by the hydrochlorination/direct chlorination process. Methylene chloride and chloroform are the desired products of this process. Carbon tetrachloride is basically a by-product of the process and is finished for sale as a product at only two facilities, the LCP Chemicals facility in Moundsville, West Virginia and the Diamond Shamrock facility in Belle, West Virginia. At other facilities, the crude by-product CCl_4 is typically used as a feed to the hydrocarbon chlorinolysis process. Since all of the products of this process are chlorinated methanes, it is generally referred to as the chloromethanes process. This label will be used in the following sections for ease of discussion.

3.3.1 Process Description

The most common feedstock for this process is methanol. The methanol is hydrochlorinated with hydrogen chloride to form methyl chloride as shown below:

$$\underset{\text{(methanol)}}{CH_3OH} + \underset{\text{(hydrochloric acid)}}{HCl} \xrightarrow[\text{(340°C)}]{\text{catalyst}} \underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{water}}{H_2O}$$

Zinc chloride on pumice, cuprous chloride, or activated charcoal is used as catalyst.[5] The methyl chloride vapor phase is quenched, washed with caustic soda solution to remove traces of hydrogen chloride, and dried with sulfuric acid prior to storage. The methyl chloride from storage is then directly chlorinated to produce methylene chloride, chloroform and carbon tetrachloride. Reactions occurring in the thermal chlorinator are:

$$\underset{\text{(methyl chloride)}}{CH_3Cl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(methylene chloride)}}{CH_2Cl_2} + \underset{\text{(hydrochloric acid)}}{HCl}$$

$$\underset{\text{(methylene chloride)}}{CH_2Cl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(hydrochloric acid)}}{HCl}$$

$$\underset{\text{(chloroform)}}{CHCl_3} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(carbon tetrachloride)}}{CCl_4} + \underset{\text{(hydrochloric acid)}}{HCl}$$

Methane may also be used as a feed material. In this case, the first reactor is not used. The hydrogen chloride produced in these reactions is either used in the hydrochlorination reactor or sold as anhydrous HCl. Products from the thermal chlorinator are quenched and then separated by distillation. A schematic of the process is presented in Figure 3-3.

3.3.2 Current Controls and Emissions

The primary types of emissions from this process are process vent, equipment leak, and storage emissions. In addition, relatively small emissions occur from equipment openings, emergency relief device discharges, secondary sources, and from loading at two facilities. A summary of estimated emissions by facility and type is presented in Table 3-2. Total emissions from all facilities using the chloromethanes process is estimated to be 78.7 Mg/yr.

The estimated emissions for each facility along with present controls are presented in Table 3-4 by individual emission source. All information presented in Table 3-4 is based on company responses to Section 114 requests. Methods used to estimate emissions from company supplied data are presented in Appendix B.

As presented in Tables 3-2 and 3-4, total estimated emissions at individual facilities range from 0.7 Mg/yr to 29.5 Mg/yr. The relatively broad range in emissions results from the difference in reported process emissions and equipment count information used for estimating equipment leak emissions. LCP Chemicals in Moundsville, West Virginia, with the highest total emissions (29.5 Mg/yr) reported process vent emissions of 11.8 Mg/yr compared to 0.7 Mg/yr or less for other facilities. Also, the reported number of potential equipment leak sources (i.e., pumps, valves, compressors, flanges) in CCl_4 service vary widely causing estimated CCl_4 equipment leak emissions to range from 3.95 Mg/yr to 26.2 Mg/yr. In addition, the equipment counts for the Vulcan facility in Wichita, Kansas, were not supplied separately. Instead, the combined equipment counts for both the hydrocarbon chlorinolysis and chloromethanes process were supplied. Rather than attempting to apportion equipment leak emission estimates to each of the two processes, the combined emission estimate was presented in the previous Section (3.2.2) for the hydrocarbon chlorinolysis process.

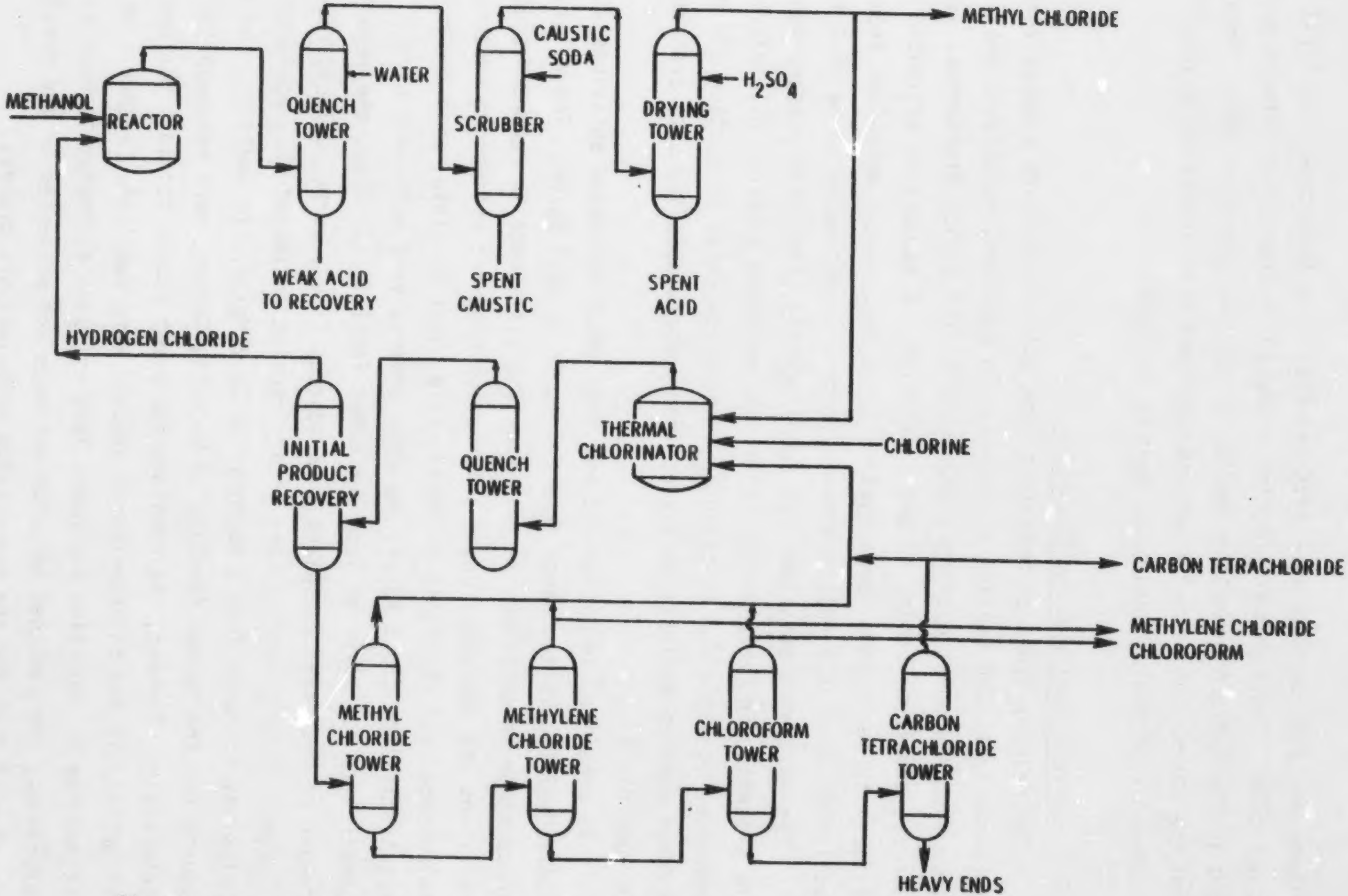
METHANOL
REACTOR
QUENCH TOWER
WATER
WEAK ACID TO RECOVERY
SCRUBBER
CAUSTIC SODA
SPENT CAUSTIC
DRYING TOWER
H_2SO_4
SPENT ACID
METHYL CHLORIDE
HYDROGEN CHLORIDE
INITIAL PRODUCT RECOVERY
QUENCH TOWER
THERMAL CHLORINATOR
CHLORINE
CARBON TETRACHLORIDE
METHYLENE CHLORIDE
CHLOROFORM
METHYL CHLORIDE TOWER
METHYLENE CHLORIDE TOWER
CHLOROFORM TOWER
CARBON TETRACHLORIDE TOWER
HEAVY ENDS

Figure 3-3. Carbon tetrachloride by the hydrochlorinaton/direct chlorination process.

TABLE 3-4. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT FACILITIES PRODUCING CARBON TETRACHLORIDE BY THE HYDROCHLORINATION/DIRECT CHLORINATION PROCESS

Company/Location	Type of Emission	Present Controls	Control Efficiency	Present CCl_4 Emissions (Mg/yr)	Comments
LCP Chemicals and Plastics/[15] Moundsville, WV	Process Vents				Continuous
	- CM 07 Purge Condenser	Compression & Condensation	98[a]	0.1	Continuous
	- CM 15 CCl_4 Dist. Vent	Condenser	84	9.52	Continuous
	- CM 16 Recovery Tank	None	0	0.56	Continuous
	- CM 18 CH_2 Cl_2 Bottoms Tank	None	0	0.71	Continuous
	- CM 22 $CHCl_3$ Tray Draw	None	0	0.90	Continuous
	Pressure Relief Devices	None	0	N/A	8 discharges of unknown quantity
	Equipment Leak	Fixed point sampling once per shift	0	14.3	
	Storage				
	- Fixed-Roof Tank	None	0	0.60	10,000 gallon
	- Fixed-Roof Tank	None	0	0.60	10,000 gallon
	Handling				
	- Rail Cars	None	0	1.92	
	Secondary				
	1	Distillation & Recovery	unknown	0.09	Assumed 0 control efficiency
	2	Neutralization & Carbon Ads	unknown	0.09	Assumed 0 control efficiency
	3	None	0	unknown	
	4	Off-site disposal	unknown	0.11	Assumed 0 control efficiency
	TOTAL			29.5	
Diamond Shamrock/[16] Belle, WV	Process Vents				
	- VR-1	Condenser	88.7	0.05	Continuous
	- Regeneration Vent	None	0	0.19	Intermittent
	Pressure Relief Devices	None	0	0.05	1 disharge in 1983
	Equipment Leak	None	0	26.2	
	Equipment Openings	None	0	0.05	12 openings
	Storage				
	- Fixed-roof Tank	Condenser	62.4	0.01	15,000 gallon, 0.99% CCl_4
	- Fixed-roof Tank	Condenser	62.4	0.01	15,000 gallon, 0.99% CCl_4
	- Fixed-roof Tank	None	0	0.08	12,000 gallon, 5.0 % CCl_4
	- Fixed-roof Tank	Condenser	24.7	0.37	17,000 gallon, 98.0% CCl_4
	- Fixed-roof Tank	Condenser	41.9	0.025	20,000 gallon, 0.89% CCl_4
	- Fixed-roof Tank	Condenser	41.9	0.025	20,000 gallon, 0.89% CCl_4
	- Fixed-roof Tank	None	0	0.0005	250 gallon, 2% CCl_4

TABLE 3-4. (Continued)

Company/Location	Type of Emission	Present Controls	Control Efficiency	Present CCl_4 Emissions (Mg/yr)	Comments
Diamond Shamrock (Cont'd)	Handling				
	- Rail Cars	None	0	0.1	
	Secondary				
	- Waste treatment effluent	Steam Strip/Carbon Ads	NR	0.001	
	- Drumming solid waste	Land Fill	NR	1.5	
	TOTAL			28.7	
Dow Chemical/[7] Freeport, TX	Process Vents				
	*	*	*	<0.001	
	Equipment Leak	None	0	5.73	
	Equipment Openings	None	0	0.01	28 openings
	Storage				
	*	*	*	0.02	
	Secondary				
	- Spent Filter Tubes	Incinerator	98[b]	<0.001	
	- Spent Adsorbant	Incinerator	98[b]	0.03	
	TOTAL			5.8	
Dow Chemical/[8] Plaquemine, LA	Process Vent				
	- T-803 Scrubber	None	0	0.20	Intermittent, 4 times/ yr for 10 minutes
	Equipment Leak	Fixed Point Monitors	0	3.95	
	Equipment Openings	None	0	0.05	2 openings
	Storage				
	- Fixed Roof Tank	None	0	0.98	10,000 gal, 60% CCl_4
	TOTAL			5.1	
Vulcan Materials/[10] Geismar, LA	Process Vents				
	- D-518A Solvent Rerun Tank	N_2 Pad	NR	0.35	Each vents 50% of the time
	- D-518B Solvent Rerun Tank	N_2 Pad	NR	0.35	
	Equipment Leak	None	0	8.18	
	TOTAL			8.9	

TABLE 3-4. (Continued)

Company/Location	Type of Emission	Present Controls	Control Efficiency	Present CCl_4 Emissions (Mg/yr)	Comments
Vulcan Materials/[11] Wichita, KS	Process Vents				
	*	*	*	0.71	
	*	*	*	0.01	
	TOTAL			0.72	

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[a] Company reported greater than 98 percent control, but only 98 percent is accepted without supporting test data.

[b] Estimated control efficiency. Not reported by company.

NR = Not Reported

* = Confidential

All facilities producing CCl_4 by the chloromethanes process reported process vent emissions. The total estimated CCl_4 emissions for all facilities is 13.6 Mg/yr. The majority of these emissions were reported by one facility, LCP Chemicals in Moundsville, West Virginia. Process vent emissions at this facility are estimated to be 11.8 Mg/yr from five vents. Two of these vents are presently controlled. One process vent is controlled greater than 98 percent by compression and condensation. Another process vent is controlled 84 percent by a condenser, but is still the highest emitting process vent. One process vent is also controlled by a condenser (88.7 percent) at the Diamond Shamrock facility in Belle, West Virginia. Two facilities do not control any process vents. Two facilities, Dow/Freeport and Vulcan/Wichita, consider all information on process vents confidential.

Three facilities are subject to State regulations for process vents. Two facilities, Dow/Plaquemine and Vulcan/Geismar, are located in Louisiana. Louisiana requires control of process vent emissions by incineration, carbon adsorption, or refrigeration. However, the control requirements may be waived if the stream is less than 100 tons/yr, will not support combustion without auxiliary fuel, or cause economic hardship. Process vents from these two facilities meet the first two criteria for obtaining a waiver. Texas requires incineration or an approved substitute control for facilities located in Brazoria County. But, there is an exemption for process vents emitting less than 45.4 Kg/24 hrs (100 lbs/24 hrs). Therefore, the Dow/Freeport facility is exempt from process vent control requirements.

Equipment leak emissions account for the majority of the estimated total emissions from facilities using the chloromethanes process. About 58.4 Mg or 74 percent of estimated annual CCl_4 emissions are from equipment leaks. Presently, none of the facilities have a formal program for control of equipment leak emissions. Two facilities reported the use of fixed point monitors to help identify leaks, but the effectiveness of these practices is unknown and expected to be minimal.

Two of the facilities are affected by recent regulations enacted in Louisiana requiring control of equipment leak emissions. The final compliance date for this regulation is December 31, 1987. Requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and liquid valves, monthly leak detection for compressor seals, and capping of open-end lines. A reasonable effort to repair identified leaking components is required within 15 days.

Only three of the six facilities reported CCl_4 storage tanks. Since CCl_4 is basically a by-product in the chloromethanes process, these tanks are relatively small, 20,000 gallons or less. The total estimated emissions from storage tanks is 2.7 Mg of CCl_4. Controls presently employed include condensers on five of the six storage tanks at the Diamond Shamrock facility in Belle, West Virginia. Only one storage tank is located in a State with regulations on storage tank emissions. This tank, at Dow/Freeport is below the size exemption of 40,000 gallons but is still controlled.

Two facilities reported emissions from loading product CCl_4 into railcars. LCP Chemicals in Moundsville, West Virginia, reported loading emissions of 1.9 Mg/yr and Diamond Shamrock in Belle, West Virginia, reported loading emissions of 0.1 Mg/yr. At all the other facilities, CCl_4 produced in the chloromethanes process is used as feed to the hydrocarbon chlorinolysis process. Therefore, there are no loading emissions.

Other sources of emissions from facilities using the chloromethanes process are pressure relief device discharges, opening of equipment for maintenance and secondary emissions from handling and treatment of waste streams. These sources account for only about 1.8 Mg or 2 percent of annual CCl_4 emissions from chloromethanes production facilities. There are no applicable State regulations governing these emission sources.

3.4 CARBON DISULFIDE PROCESS

There is currently one CCl_4 facility using the carbon disulfide process. This facility is located near LeMoyne, Alabama. It is owned and operated by Stauffer Chemical and accounts for 17 percent of U.S. CCl_4 production. It also accounts for 306 Mg or about 34 percent of the estimated total annual emissions from CCl_4 production facilities. These emissions are expected to increase when additional capacity is added in 1985.

3.4.1 Process Description

In the carbon disulfide process, carbon disulfide is fed to the primary reactor along with sulfur monochloride. A schematic of the process is presented in Figure 3-4. The following reaction takes place in the primary reactor:

$$\underset{\text{(carbon disulfide)}}{CS_2} + \underset{\text{(sulfur monochloride)}}{2S_2Cl_2} \longrightarrow \underset{\text{(sulfur)}}{6S} + \underset{\text{(carbon tetrachloride)}}{CCl_4}$$

Unreacted carbon disulfide from the primary reactor is subsequently chlorinated in the chlorinator reactor in the presence of divided iron catalyst. The following reaction occurs:

$$\underset{\text{(carbon disulfide)}}{CS_2} + \underset{\text{(chlorine)}}{3Cl_2} \longrightarrow \underset{\text{(sulfur monochloride)}}{S_2Cl_2} + \underset{\text{(carbon tetrachloride)}}{CCl_4}$$

Effluents from the chlorinator reactor are distilled to separate crude product as overhead. Molten sulfur containing some sulfur monochloride is removed as bottoms. The sulfur is separated with the "equivalent to fresh" sulfur going to the carbon disulfide plant as feed and residual sulfur going to the sulfur chlorinator. The residual sulfur stream is directly chlorinated to form sulfur monochloride for the primary reactor. Crude CCL_4 from the crude distillation column is neutralized and then further distilled to obtain product CCl_4.[5]

3.4.2 Current Controls and Emissions

Stauffer reported process vent, fugitive, storage, loading, equipment opening and secondary emissions. Emission quantities from each of these sources are summarized in Table 3-2. Total CCl_4 emissions from this facility are estimated to be 305.6 Mg/yr.

There are three process vents at the Stauffer facility with reported CCl_4 emissions. Estimated emission quantities for each of these vents are presented in Table 3-5. Total process vent emissions are reportedly 138.9 Mg

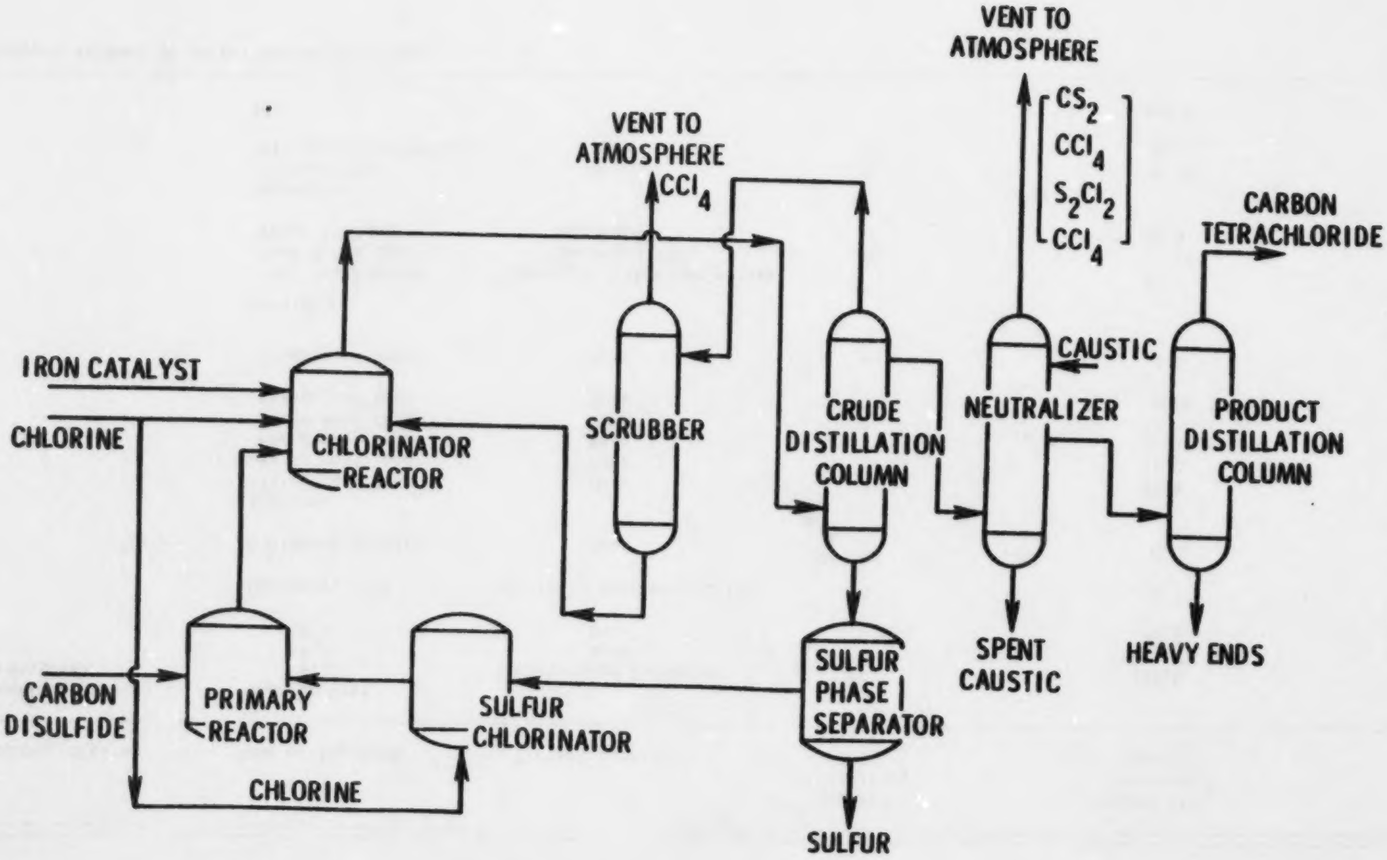
VENT TO ATMOSPHERE
CS2
CCl4
S2Cl2
CCl4
VENT TO ATMOSPHERE
CCl4
CARBON TETRACHLORIDE
IRON CATALYST
CHLORINE
CHLORINATOR REACTOR
SCRUBBER
CRUDE DISTILLATION COLUMN
CAUSTIC
NEUTRALIZER
PRODUCT DISTILLATION COLUMN
CARBON DISULFIDE
PRIMARY REACTOR
SULFUR CHLORINATOR
SULFUR PHASE SEPARATOR
SPENT CAUSTIC
HEAVY ENDS
CHLORINE
SULFUR

Figure 3-4. Carbon tetrachloride by the carbon disulfide process.

TABLE 3-5. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT FACILITIES PRODUCING CARBON TETRACHLORIDE BY THE CARBON DISULFIDE PROCESS

Company/Location	Type of Emission	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Stauffer Chemical LeMoyne/Al	Process Vent				
	CT-1	Refrigerated Condenser	98	111.5	Continuous
	CT-3	None	0	.9	Continuous
	CT-5	None	0	26.5	Continuous
	Equipment Leak	Quarterly Area Monitoring	0	74.2	
	Equipment Opening	None	0	0.04	213 Openings
	Storage				
	Fixed roof tank	None	0	11.0	233,000 gallon
	Fixed roof tank	None	0	11.0	233,000 gallon
	Fixed roof tank	None	0	21.1	460,000 gallon
	Fixed roof tank	None	0	21.1	460,000 gallon
	Fixed roof tank	None	0	0.66	18,000 gallon, 80% CCl_4
	Fixed roof tank	None	0	1.6	18,000 gallon, 80% CCl_4
	Handling				
	Tank Car Loading	Submerged fill/vapor return	0[a]	12.7	
	Tank Truck Loading	Submerged fill	0[a]	.16	
	Barge Loading	Submerged fill	0[a]	12.9	
	Secondary				
	Effluent Pit	None	0	>0.001	
	Oil Recovery Effluent	None	0	0.2	
	TOTAL			305.6	

[a] Company assumed 0% in estimating emissions.

of CCl_4 annually accounting for 45 percent of total plant emissions. The majority of process vent emissions are from one vent with reported annual emissions of 111.5 Mg of CCl_4 after the control device. This emission source is presently controlled by a refrigerated condenser with a reported efficiency of 98 percent. The other two process vent emissions are uncontrolled. There are no State or local regulations requiring control of these process vent emissions.

Based on equipment counts provided by Stauffer, equipment leak emissions are estimated to be 74.2 Mg/yr. Stauffer currently does not have any program for control of equipment leak emissions. Stauffer did report that area monitoring is performed monthly which is claimed to aid in leak detection. The control efficiency of this practice is unknown and expected to be minimal. The State of Alabama does not have any regulations requiring control of equipment leak emissions at this facility.

There are six uncontrolled fixed-roof storage tanks at the Stauffer facility. These tanks range in size from 18,000 gallons to 460,000 gallons. Four of the storage tanks contain greater than 99 percent pure CCl_4, while two tanks are used to store an 80:20 mixture of CCl_4 and carbon disulfide. Estimated emissions based on 1983 storage tank data are presented in Table 3-5 for each tank. It should be noted that the 80:20 mixture stored in two of the tanks was for use as a grain fumigant. The use of CCl_4 in grain fumigants has recently been banned by the EPA.[18] These tanks are likely to be used for storage of pure CCl_4, especially with current plans to boost production in 1985. This will result in higher CCl_4 storage emissions.

Total 1983 CCl_4 emissions from storage tanks at the Stauffer facility are estimated to be 66.5 Mg. Therefore, storage emissions account for about 22 percent of total emissions from this facility. Currently, there are no State regulations requiring control of these storage tanks.

Stauffer estimated that a total of 25.8 Mg of CCl_4 is emitted from loading of tank cars, tank trucks, and barges in 1983. All of these loading operations are presently uncontrolled. The major sources are from tank car and barge loading with estimated annual emissions of 12.7 Mg and 12.9 Mg, respectively. There are no State regulations affecting loading emissions at this facility.

Stauffer reported 213 openings of process equipment in 1983. The estimated emissions from these openings is 0.04 Mg. These emissions are currently uncontrolled and are not subject to any State regulatory requirements.

Two sources of secondary emissions were reported by Stauffer. An estimated 1 kg of CCl_4 is emitted from the effluent pit and an estimated 0.2 Mg of CCl_4 is emitted from the oil recovery effluent in 1983. Neither of these sources is controlled or subject to any regulatory requirements.

3.5 COST OF ADDITIONAL CONTROLS

Cost estimates were developed for control of process vent, equipment leak, storage, and loading emission sources not presently well controlled. The cost effectiveness to control each of these emission sources at facilities producing carbon tetrachloride are presented in Table 3-6 and discussed in the following sections. Methods used for estimating costs are presented in Appendix C.

The achievable emission reduction for different VOC cost effectiveness ranges is presented in Table 3-7. These emission reductions can be compared to total estimated CCl_4 emissions of 898 Mg in 1983 (presented in Table 3-2).

3.5.1 Control of Process Vent Emissions

Cost estimates were developed for controlling process emissions by incineration for vents not presently controlled 98 percent or better. These estimates along with the estimated cost effectiveness are presented in Table 3-6. As presented in Table 3-6, the estimated cost effectiveness of controlling process vent emissions ranges from $1,330/Mg of VOC to over $2,000,000/Mg of VOC. The range of estimated CCl_4 cost effectiveness is $3,800/Mg of CCl_4 to over $2,000,000/Mg of CCl_4. As shown in Tables 3-6 and 3-7, process vent emissions can be controlled for less than $5000/Mg of VOC at only one facility, Stauffer in LeMoyne, Alabama. This is the only facility using the carbon disulfide process. Control of process vent emissions at this facility is estimated to cost $1330/Mg of VOC and would result in a

TABLE 3-6. COSTS OF ADDITIONAL CONTROLS FOR CARBON TETRACHLORIDE PRODUCTION FACILITIES

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
HYDROCARBON CHLORINOLYSIS PROCESS								
E.I. duPont/ Corpus Christi, TX	Process Vents	Incinerator	16.0/16.0	3,676.0	0.0	2,747.6	172,000	172,000
	Equipment Leak	Equipment and Work Practices	33.4/44.8	35.3	14.8	23.0	690	510
	Storage - Fixed Roof Tank	Condenser	0.1/0.1	110.8	0.0	29.1	228,000	228,000
	Loading - Ships & Barges	Incinerator	4.4/4.4	1,209.0	0.0	409.4	93,000	93,000
Dow Chemical/ Freeport, TX	Process Vents	Incinerator	28.9/43.8	1,219.0	0.0	414.1	14,300	9,450
	Equipment Leak	Equipment Work and Practices	36.0/48.7	74.8	16.1	32.6	900	670
	Storage - Fixed-Roof Tank	Floating Roof-PO	1.8/1.8	19.7	0.6	4.6	2,570	2,570
		Floating Roof-SS	1.8/1.8	22.8	0.6	5.4	2,980	2,980
		Refrigerated Condenser	1.4/1.4	110.8	0.5	28.6	20,100	20,100
	- Fixed-Roof Tank	Floating Roof-PO	0.1/0.1	11.4	0.0	3.0	24,000	24,000
		Floating Roof-SS	0.1/0.1	12.9	0.0	3.3	23,600	23,400
		Refrigerated Condenser	0.3/0.3	110.8	0.1	29.0	95,100	94,200
	- Loading	Ships & Barges	1.2/1.2	1,209.0	0.0	409.5	348,000	348,000
		Tank Cars, Tank Truck & Drums	1.8/1.8	1,209.0	0.0	409.7	221,000	221,000
Dow Chemical/ Plaquemine, LA	Process Vents	Incinerator	8.8/8.8	1,219.0	0.0	525.4	59,700	59,700
	Equipment Leak	Equipment and Work Practices	49.6/101.7	288.4	33.5	61.1	1,230	600
	Loading - Barges	Incinerator	5.6/5.6	1,209.0	0.0	409.6	73,800	73,800
	- Tank Cars & Trucks	Incinerator	11.1/11.1	1,209.0	0.0	409.7	37,000	37,000

TABLE 3-6. (Continued)

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness CCl_4 ($/Mg)	Cost Effectiveness VOC ($/Mg)
Dow Chemical/ Pittsburg, CA	Storage							
	- Fixed-Roof Tank	Floating Roof-PO	2.1/2.1	15.4	0.7	3.3	1,540	1,540
		Floating Roof-SS	2.2/2.2	17.6	0.7	3.9	1,800	1,800
		Refrigerated Condenser	2.2/2.1	110.8	0.7	28.4	12,600	12,500
	- Fixed-Roof Tank	Floating Roof-PO	2.1/2.2	15.4	0.7	3.3	1,500	1,500
		Floating Roof-SS	2.2/2.2	17.6	0.7	3.9	1,800	1,800
		Refrigerated Condenser	2.2/2.2	110.8	0.7	28.4	12,600	12,500
	- Fixed-Roof Tank	Floating Roof-PO	14.8/15.0	54.0	4.9	9.2	600	600
		Floating Roof-SS	15.0/15.2	63.0	5.0	11.5	800	800
		Refrigerated Condenser	13.7/13.8	110.8	4.5	24.6	1,800	1,800
	Loading							
	- Tank Cars, Tank	Incinerator	6.2/6.2	1,209.0	0.0	409.8	66,100	66,100
Vulcan Materials/ Geismar, LA	Process Vents	Incinerator	6.4/6.4	1,257.0	0.0	423.9	66,200	66,200
	Equipment Leak	Equipment and Work Practices	37.2/63.3	130.0	20.9	38.8	1,000	600
	Storage							
	- *	Int. Floating Roof-PO	3.0/3.0	42.7	1.0	10.2	3,400	3,400
		Int. Floating Roof-SS	3.0/3.0	50.2	1.0	12.2	4,000	4,000
		Refrigerated Condenser	1.2/1.2	110.8	0.4	28.7	24,000	24,000
	- *	Int. Floating Roof-PO	5.1/5.1	88.6	1.7	21.6	4,250	4,250
		Int. Floating Roof-SS	5.2/5.2	104.6	1.7	25.8	5,000	5,000
		Refrigerated Condenser	2.2/2.2	110.8	0.7	28.4	13,000	13,000
	Loading							
	- Ships & Barges	Incinerator	0.3/0.3	1,209.0	0.0	409.4	1,250,000	1,250,000
Vulcan Materials/ Wichita, KS	Process Vents	Incinerator	0.4/0.4	1,209.0	0.0	409.4	1,130,000	1,130,000
	Equipment Leak	Equipment and Work Practices	52.8/82.7	43.0	27.3	26.9	500	300
	Storage							
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.5/0.5	15.1	0.2	3.8	6,700	6,700
		Int. Floating Roof-SS	0.6/0.6	17.4	0.2	4.4	7,500	6,500
		Refrigerated Condenser	0.7/0.7	110.8	0.2	28.9	41,800	41,800

TABLE 3-6. (Continued)

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Vulcan Chemicals/ Wichita, KS (Cont.)	- Fixed-Roof Tank	Int. Floating Roof-PO	0.5/0.5	15.1	0.2	3.8	6,700	6,700
		Int. Floating Roof-SS	0.6/0.6	17.4	0.2	4.4	7,500	7,500
		Refrigerated Condenser	0.7/0.7	110.8	0.2	28.9	41,800	41,800
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.5/0.5	13.3	0.2	3.3	6,200	6,200
		Int. Floating Roof-SS	0.5/0.5	15.2	0.2	3.8	6,900	6,900
		Refrigerated Condenser	0.6/0.6	110.8	0.2	28.9	43,200	43,200
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.5/0.5	13.3	0.2	3.3	6,200	6,200
		Int. Floating Roof-SS	0.5/0.5	15.2	0.2	3.8	6,900	6,900
		Refrigerated Condenser	0.6/0.6	110.8	0.2	28.9	43,200	43,200
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.7/1.4	23.1	0.4	5.6	8,300	4,100
		Int. Floating Roof-SS	0.7/1.4	26.8	0.5	6.6	9,400	4,700
		Refrigerated Condenser	0.7/1.4	110.8	0.5	28.7	40,500	20,200
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.0/0.0	13.0	0.0	3.4	898,100	89,800
		Int. Floating Roof-SS	0.0/0.1	14.8	0.0	3.9	698,900	69,900
		Refrigerated Condenser	0.0/0.2	110.8	0.1	29.0	1,321,000	132,100
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.1/0.2	13.4	0.1	3.4	27,800	13,900
		Int. Floating Roof-SS	0.1/0.3	15.3	0.1	3.9	29,600	14,800
		Refrigerated Condenser	0.2/0.4	110.8	0.1	29.0	143,900	72,000
	- Fixed-Roof Tank	Int. Floating Roof-PO	11.2/11.2	56.2	3.7	11.1	1,000	1,000
		Int. Floating Roof-SS	11.3/11.3	65.9	3.7	13.6	1,200	1,200
		Refrigerated Condenser	10.1/10.1	110.8	3.3	25.8	2,600	2,600
	Loading - Tank Cars, Tank Trucks, & Drums	Incinerator	0.6/0.6	1,209.0	0.0	409.4	680,000	680,000
HYDROCHLORINATION/DIRECT CHLORINATION PROCESS								
LCP Chemicals & Plastics/ Moundsville, WV	Process Vents	Incinerator	11.5/20.4	1,257.0	0.0	423.5	36,800	20,800
	Equipment Leak	Equipment and Work Practices	8.9/49.0	122.7	16.2	31.8	3,600	650
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	0.3/0.3	15.1	0.1	3.9	12,200	12,200
		Int. Floating Roof-SS	0.3/0.3	17.4	0.1	4.4	13,000	13,000
		Refrigerated Condenser	0.5/0.5	110.8	0.1	28.9	57,400	57,400

TABLE 3-6. (Continued)

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness CCl_4 ($/Mg)	Cost Effectiveness VOC ($/Mg)
LCP Chemicals & Plastics/ Moundsville, WV (Cont'd)	- Fixed-Roof Tank	Int. Floating Roof-PO	0.3/0.3	15.1	0.1	3.9	12,200	12,200
		Int. Floating Roof-SS	0.3/0.3	17.4	0.1	4.4	13,000	13,000
		Refrigerated Condenser	0.5/0.5	110.8	0.1	28.9	57,400	57,400
	Loading							
	- Tank Cars	Incinerator	1.9/1.9	1,209.0	0.0	409.4	215,200	215,200
Diamond Shamrock/ Belle, WV	Process Vents	Incinerator	0.2/0.2	1,209.0	0.0	409.4	2,102,510	2,102,510
	Equipment Leak	Equipment and Work Practices	13.4/75.1	58.8	24.8	36.3	2,700	500
	Storage							
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.0/0.9	14.7	0.3	3.6	412,400	4,100
		Int. Floating Roof-SS	0.0/0.9	16.9	0.3	4.1	472,500	4,700
		Refrigerated Condenser	0.0/0.6	110.8	0.2	28.9	4,795,400	47,700
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.0/0.9	14.7	0.3	3.6	412,400	4,100
		Int. Floating Roof-SS	0.0/0.9	16.9	0.3	4.1	472,500	4,700
		Refrigerated Condenser	0.0/0.6	110.8	0.2	28.9	4,795,400	47,500
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.1/1.3	11.5	0.4	2.6	41,200	2,100
		Int. Floating Roof-SS	0.1/1.3	13.0	0.4	3.0	46,600	2,300
		Refrigerated Condenser	0.1/1.3	110.8	0.4	28.7	429,800	21,500
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.2/0.2	12.5	0.1	3.2	17,500	17,100
		Int. Floating Roof-SS	0.2/0.2	14.2	0.1	3.7	18,400	18,100
		Refrigerated Condenser	0.3/0.3	110.8	0.1	29.0	97,800	95,800
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.0/2.7	15.3	0.8	3.2	137,600	1,200
		Int. Floating Roof-SS	0.0/2.7	17.6	0.8	3.7	162,200	1,400
		Refrigerated Condenser	0.0/2.1	110.8	0.7	28.4	1,502,500	13,400
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.0/2.7	15.3	0.8	3.2	137,600	1,200
		Int. Floating Roof-SS	0.0/2.7	17.6	0.8	3.7	162,200	1,400
		Refrigerated Condenser	0.0/2.1	110.8	0.7	28.4	1,502,500	13,400
	- Fixed-Roof Tank	Refrigerated Condenser	Cost Effectiveness Exceeds $1,000,000/Mg VOC					
	Loading	Incinerator	0.1/0.1	1,209.0	0.0	409.0	4,100,000	4,100,000

TABLE 3-6. (Continued)

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Dow Chemical Freeport, TX	Equipment Leak	Equipment and Work Practices	3.7/10.4	13.9	3.4	10.2	2,800	1,000
Dow Chemical/ Plaquemine, LA	Process Vents	Incinerator	0.2/0.2	1,209.0	0.0	409.4	2,102,500	2,102,500
	Equipment Leak	Equipment and Work Practices	2.4/2.7	15.4	0.9	9.4	4,000	3,500
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	0.7/1.2	13.4	0.4	3.1	4,300	2,600
		Int. Floating Roof-SS	0.7/1.2	15.3	0.4	3.6	4,800	2,800
		Refrigerated Condenser	0.8/1.4	110.8	0.5	28.7	34,500	20,700
Vulcan Materials/ Geismar, LA	Process Vents	Incinerator	0.7/0.7	1,219.0	0.0	412.3	590,000	590,000
	Equipment Leak	Equipment and Work Practices	4.2/30.6	37.1	10.1	21.3	5,100	700
Vulcan Materials/ Wichita, KS	Process Vents	Incinerator	0.7/0.7	1,219.0	0.0	412.2	575,600	575,600
CARBON DISULFIDE PROCESS								
Stauffer Chemical/ LeMoyne, AL	Process Vents	Incinerator	136.1/349.6	1,219.8	0.0	466.3	3,420	1,330
	Equipment Leak	Equipment and Work Practices	31.6/46.9	40.4	15.5	22.1	700	500
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	10.1/10.1	40.8	3.3	7.4	700	700
		Int. Floating Roof-SS	10.2/10.2	47.8	3.4	9.1	900	900
		Refrigerated Condenser	9.3/9.3	110.8	3.1	26.0	2,800	2,800
	- Fixed-Roof Tank	Int. Floating Roof-PO	10.1/10.1	40.8	3.3	7.4	700	700
		Int. Floating Roof-SS	10.2/10.2	47.8	3.4	9.1	900	900
		Refrigerated Condenser	9.3/9.3	110.8	3.1	26.0	2,800	2,800
	- Fixed-Roof Tank	Int. Floating Roof-PO	19.9/19.9	56.1	6.5	8.1	400	400
		Int. Floating Roof-SS	20.0/20.0	65.8	6.6	10.7	500	500
		Refrigerated Condenser	17.9/17.9	110.8	5.9	23.2	1,300	1,300

TABLE 3-6. (Continued)

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Stauffer Chemical/ LeMoyne, AL (Cont'd)	- Fixed-Roof Tank	Int. Floating Roof-PO	19.9/19.9	56.1	6.5	8.1	400	400
		Int. Floating Roof-SS	20.0/20.0	65.8	6.6	10.7	500	500
		Refrigerated Condenser	17.9/17.9	110.8	5.9	23.2	1,300	1,300
	- Fixed-Roof Tank	Int. Floating Roof-PO	0.3/0.4	13.5	0.1	3.4	9,900	7,900
		Int. Floating Roof-SS	0.4/0.5	15.4	0.2	3.9	10,500	8,400
		Refrigerated Condenser	0.6/0.7	110.8	0.2	28.9	51,600	41,300
	- Fixed-Roof Tank	Int. Floating Roof-PO	1.3/1.6	13.5	0.5	3.0	2,300	1,900
		Int. Floating Roof-SS	1.3/1.7	15.4	0.5	3.5	2,600	2,100
		Refrigerated Condenser	1.4/1.7	110.8	0.6	28.5	20,700	16,500
	Loading							
	- Tank Cars	Incinerator	12.4/12.4	1,209.0	0.0	413.5	33,300	33,300
	- Barges	Incinerator	12.6/12.6	1,209.0	0.0	410.4	32,600	32,600

PO - Primary Seal Only.
SS - Primary and Secondary Seals.

TABLE 3-7. ACHIEVABLE CCl_4 EMISSION REDUCTION AT CARBON TETRACHLORIDE PRODUCTION FACILITIES (Mg/Yr)

Cost Effectiveness Range $/Mg of VOC	Process Vents	Equipment Leak	Storage[a] Tanks	Loading	Total
HYDROCARBON CHLORINOLYSIS PROCESS					
Credit	-	-	-	-	-
0 - 500	-	52.8	-	-	52.8
500 - 1,000	-	156.2	26.0	-	182.2
1,000 - 2,000	-	-	4.2	-	4.2
2,000 - 5,000	-	-	10.6	-	10.6
>5,000	60.5	-	2.3	31.2	94.0
SUBTOTAL	60.5	209.0	43.1	31.2	343.8
HYDROCHLORINATION/DIRECT CHLORINATION PROCESS					
Credit	-	-	-	-	-
0 - 500	-	13.4	-	-	13.4
500 - 1,000	-	16.8	-	-	16.8
1,000 - 2,000	-	-	0.0[b]	-	0.0[b]
2,000 - 5,000	-	2.4	0.8	-	3.2
>5,000	13.3	-	0.8	2.0	16.1
SUBTOTAL	13.3	32.6	1.6	2.0	49.5
CARBON DISULFIDE PROCESS					
Credit	-	-	-	-	-
0 - 500	-	31.6	39.8	-	71.4
500 - 1,000	-	-	20.2	-	20.2
1,000 - 2,000	136.1	-	1.3	-	137.4
2,000 - 5,000	-	-	-	-	-
>5,000	-	-	0.3	25.0	25.3
SUBTOTAL	136.1	31.6	61.6	25.0	254.3

TABLE 3-7. (Continued)

Cost Effectiveness Range $/Mg of VOC	Process Vents	Equipment Leak	Storage[a] Tanks	Loading	Total
ALL CCl_4 PRODUCTION PROCESSES					
Credit	-	-	-	-	-
0 - 500	-	97.8	39.8	-	137.6
500 - 1,000	-	173.0	46.2	-	219.2
1,000 - 2,000	136.1	-	5.5	-	141.6
2,000 - 5,000	-	2.4	11.4	-	13.8
>5,000	73.8	-	3.4	58.2	135.4
SUBTOTAL	209.9	273.2	106.3	58.2	647.6

[a] The most cost-effective option was used to developing this table.

[b] Two tanks can be controlled for less than $2000/Mg of VOC, but the CCl_4 emission reduction is negligible.

136 Mg/yr reduction of CCl_4 emissions, a 63 percent reduction in process vent emissions from all CCl_4 production facilities (214.2 Mg/yr).

3.5.2 Control of Equipment Leak Emissions

As discussed in Section 3.2, only one CCl_4 producer, Dow in Pittsburg, California, has a formal leak detection program. This facility reported very low equipment leak emissions supported by test data. Therefore, cost/cost effectiveness estimates were not developed for control of equipment leak emissions at this facility. The costs for all other facilities are presented in Table 3-6. The control techniques costed for control of equipment leak emissions are those required by the benzene fugitive national emission standard for hazardous air pollutants (NESHAP). This includes monthly leak detection and repair of pumps and valves, venting of compressor degassing reservoirs to a combustion device, installation of O-rings on safety relief valves in gas service, closed purge for sample connections, and capping of open-ended lines.

Estimated cost effectiveness for control of equipment leak emissions range from $300/Mg of VOC to $3500/Mg of VOC. Estimated CCl_4 cost effectiveness ranges from $500/Mg to $5100/Mg. As shown in Table 3-7, annual equipment leak emissions from all CCl_4 production facilities can be reduced by 98 Mg (21 percent) for less than $500/Mg of VOC and by 270 Mg (57 percent) for less than $1000/Mg of VOC. The VOC cost effectiveness exceeds $1000/Mg for only one facility.

3.5.3. Control of Storage Emissions

Cost estimates were developed for control of storage emissions from tanks not presently controlled by floating roofs, vapor recovery (85 percent control or better), or incineration. Three control options were evaluated: contact internal floating roof with primary seal only, contact internal floating roof with primary and secondary seals, and a refrigerated condenser for vapor recovery. Costs/cost-effectiveness estimates are presented in Table 3-6 for each option, if applicable. Internal floating roofs were not costed for tanks smaller than 2 meters in diameter or horizontal tanks. The estimated cost effectiveness ranges from $400/Mg of VOC to $228,000/Mg of VOC for the most cost-effective option on individual tanks. The estimated CCl_4 cost effectiveness is almost identical because these tanks store product CCl_4 typically greater than 99 percent pure. There is no direct correlation between tank size and cost effectiveness. The cost of a floating roof is nearly proportional to tank size. However, the emission reduction depends greatly of the tank throughput which is not a function of size.

Achievable storage tank emission reductions as a function of cost effectiveness are presented in Table 3-7. As shown in this table, annual storage tank emissions can be reduced by 40 Mg (30 percent) for less than $500/Mg of VOC and by 103 Mg (77 percent) for less than $5000/Mg of VOC.

3.5.4 Control of Loading Emissions

As discussed earlier, only two facilities presently have controls for loading emissions. DuPont in Corpus Christi, Texas, controls tank car loading emissions by 86 percent with a refrigerated condenser. Vulcan in Geismar, Louisiana, controls railcar and tank truck loading. The remainder of loading operations at facilities producing CCl_4 are uncontrolled. Costs and cost-effectiveness estimates were developed for each uncontrolled land and marine loading operation. It was assumed that all land loading operations can be controlled by a single incinerator and that all marine loading can be controlled by a single incinerator. The estimated costs of controlling each type of loading operation at individual facilities are presented in Table 3-6. The range of estimated VOC and CCl_4 cost effectiveness is $32,600/Mg to $4,100,000/Mg (VOC and CCl_4 cost effectiveness are the same).

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4.0 CHLOROFLUOROCARBON 11 & 12 PRODUCTION

The primary and single largest use for carbon tetrachloride (CCl_4) is as feedstock for the production of dichlorodifluoromethane (CFC 12) and trichlorofluoromethane (CFC 11). About 254,600 Mg of domestic CCl_4 produced was used as feedstock for CFC products in 1983. Currently, CFC 11 is used as a blowing agent in the manufacture of plastic foams and CFC 12 is used as a refrigerant. A list of major CFC production facilities, their locations, and total estimated production capacities is given in Table 4-1. The total production capacity of these facilities is about 466,000 Mg/yr. In 1983, total production for these facilities was 296,000 Mg for an overall industry capacity utilization of 64 percent.

4.1 PROCESS DESCRIPTION

Fluorocarbons 11 and 12 are produced by bubbling anhydrous hydrogen fluoride and carbon tetrachloride through molten antimony pentachloride catalyst. These reactions are slightly endothermic and take place in a steam-jacketed atmospheric pressure reactor at 65 to 95°C.[1] A schematic of the fluorocarbon production process is presented in Figure 4-1. The following chemical reactions occur in the reactor:

$$CCl_4 + HF \xrightarrow{SbCl_5} \underset{\text{(CFC 11)}}{CCl_3F} + HCl$$

$$CCl_4 + 2HF \xrightarrow{SbCl_5} \underset{\text{(CFC 12)}}{CCl_2F_2} + 2HCL$$

The gaseous mixture of fluorcarbon and unreacted chlorocarbon is distilled to separate and recycle the chlorocarbon to the reactor while the waste hydrogen chloride and chlorine are removed by a caustic scrubbing tower.

TABLE 4-1. CHLOROFLUOROCARBON PRODUCERS

Company	Location	CFC Production Capacity[a] (Mg/Yr)
Allied	El Segundo, CA Danville, IL	140,653
DuPont	Montague, MI Antioch, CA Deepwater, NJ	227,860
Kaiser Aluminum & Chemical	Gramercy, LA	36,298
Penwalt	Calvert City, KY	40,835
Essex/Racon	Wichita, KS	20,417

[a] From chemical synopis report - August 1982.

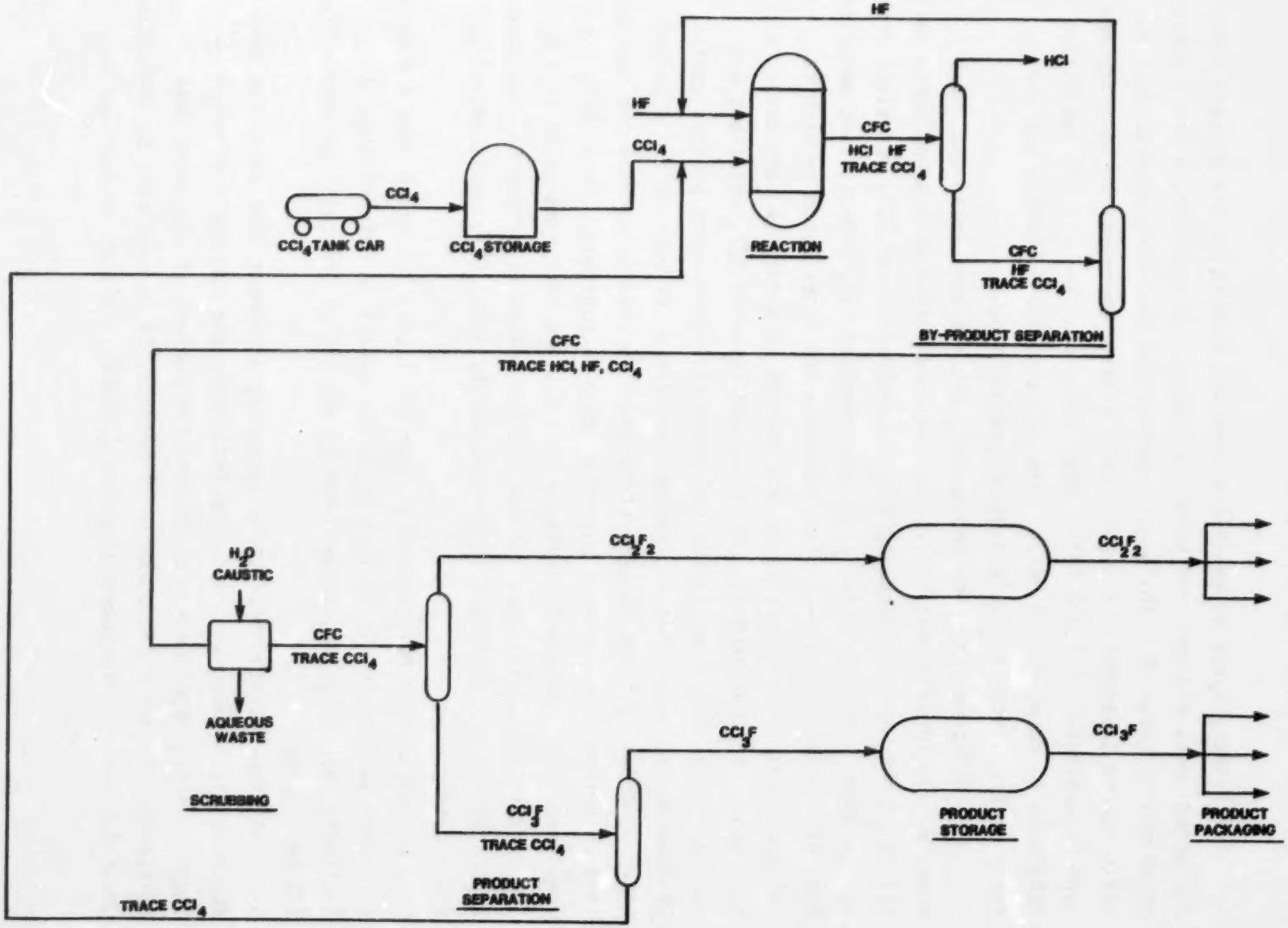
HF
HCl
HF
CCl4
CFC
HCl HF
TRACE CCl4
CCl4
CCl4 TANK CAR
CCl4 STORAGE
REACTION
CFC
HF
TRACE CCl4
BY-PRODUCT SEPARATION
CFC
TRACE HCl, HF, CCl4
H2O
CAUSTIC
CFC
TRACE CCl4
AQUEOUS WASTE
SCRUBBING
CCl2F2
CCl2F2
CCl3F
CCl3F
CCl3F
TRACE CCl4
PRODUCT SEPARATION
PRODUCT STORAGE
PRODUCT PACKAGING
TRACE CCl4

Figure 4-1. Chlorofluorocarbon 11 and 12 production.

4.2 CURRENT CONTROLS AND EMISSIONS

The primary types of emissions from CFC production are process vent, equipment leak, storage, and handling losses. In addition, a small amount of emissions occur from equipment openings and secondary sources such as waste stream treatment. A summary of estimated emissions by facility and type is presented in Table 4-2. Total emissions from all CFC facilities is estimated to be about 132 Mg/yr. The emission types/sources and their controls are listed in Table 4-3 and discussed below.

Most CFC producers reported no CCl_4 process vent emissions. For example, all three Dupont facilities reported having no process vents while Allied plants reported nondetectable concentrations of CCl_4 emissions from a HCl scrubber vent. Only two producers reported CCl_4 process vent emissions. They are Penwalt in Calvert City, Kentucky and Essex/Racon in Wichita, Kansas. Penwalt's process vents are located on a recycle tank and an air separator. Neither vent is controlled and reported CCl_4 emissions are 0.3 Mg/yr. Essex/Racon has two CFC production units with process vents located on recovery tanks and product purifiers for each unit. A packed water scrubber, with 88 percent efficiency, is used to control the recovery tank emissions. The product purifiers have no controls. Total CCl_4 process vent emissions from the Essex/Racon facility are estimated to be 13.7 Mg/yr. The process vent emissions, for the two facilities reporting CCl_4 emissions, accounted for approximately 10 percent of the total CCl_4 emissions of the CFC industry.

Equipment leak CCl_4 emissions from CFC facilities range from 4.5 Mg/yr at Dupont in Antioch, CA to 16.3 Mg/yr at Penwalt in Calvert City, KY. Equipment leak emissions account for 51 percent of the total emissions from CFC facilities.

Individual state regulations impacting equipment leak emissions vary considerably between states. Five facilities are currently affected by State or local regulatory requirements for control of equipment leak emissions. Allied's CFC plant in El Segundo, CA is regulated by the South Coast Air Quality Management District (SCAQMD). Allied is required to

TABLE 4-2. SUMMARY OF ESTIMATED 1983 CCl_4 EMISSIONS FROM CFC PRODUCTION FACILITIES (Mg)

Plant/Location	Process	Equipment Leak[a]	Equipment Openings	Storage[b]	Loading/ Handling	Secondary	Total
Allied Chemical El Segundo, CA	0	5.8	<0.01	0	0	0	5.8
Allied Chemical Danville, IL	0	7.9	0.02	0	0.18	<0.001	8.1
E.I. duPont Montague, MI	0	9.1	0.06	0.7	0.08	0.01	10.0
E.I. duPont Antioch, CA	0	4.5	0.2	6.8	0	0.03	11.5
E.I. duPont Deepwater, N.J.	0	6.1	0.04	11.6	1.7	0	19.4
Kaiser Aluminum & Chemical/ Gramercy, LA	0	12.2	1.5	0.6	1.1	0	15.4
Penwalt Calvert City, KY	0.3	16.3	9.5	12.1	0.04	0	38.2
Essex/Racon Wichita, KS	13.7	8.0	0.05	1.5	0	<0.01	23.3
TOTAL	14.0	69.9	11.4	33.3	3.1	0.05	131.8

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[a] Based on equipment count provided by plants and SOCMI equipment leak emission factors.

[b] Based on storage tank information provided by plants and AP-42 equations.

TABLE 4-3. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT CFC PRODUCTION FACILITIES

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Allied Corp/El Segundo, CA[3]	Equipment Leak	None	N/A	5.8	
	Equipment Openings - 10 Openings	None	N/A	<0.01	
	Storage - Fixed Roof Tank	Vapor Recycling	100	0	
	Loading/Handling - Tank Trucks - Rail Cars	Vapor Recovery System Vapor Recovery System	100 100	0 0	
	Secondary - Neutralization System Wastewater	None	N/A	0	
Allied Corp/Danville, IL[3]	Equipment Leak	None	N/A	7.9	
	Equipment Openings - 5 Openings	None	N/A	0.02	
	Storage - Fixed Roof	Continuous Withdrawal	100	0	163,000 gallons
	Loading/Handling - Tank Trucks & Rail Cars	Vapor Recovery System	NR	0.18	
	Secondary - Waste Stream #1	Incineration	NR	<0.001	
E.I. duPont/Montague, MI[4]	Equipment Leak	None	N/A	9.1	
	Equipment Openings - 12 Openings	None	N/A	0.06	Estimated number of openings
	Storage - Fixed Roof Tank	Vapor Balance & Cont. Process Feed[a]	NR	0	70,000 gallons
	- Fixed Roof Tank	Vapor Balance[a]	NR	0.7	50,000 gallons
	Loading/Handling - Rail Car	Vapor Balance	NR	0.08	Emissions estimated
	Secondary - Drum Wastes - NPDES Wastes	Incineration None	NR N/A	0.01 0	

TABLE 4-3. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
E.I. duPont/Antioch, CA[4]	Equipment Leak	None	N/A	4.5	
	Equipment Openings - 8 Openings	None	N/A	0.2	
	Storage - Fixed Roof Tank	Low Temp. Condenser followed$_b$by carbon adsorber^b	100^b	6.8	Present CCl_4 emissions will be eliminated with control system
	Secondary - High Boilers Waste Stream	Incineration	NR	0.02	
E.I. duPont/Deepwater, NJ[4]	Equipment Leak	None	N/A	6.1	
	Equipment Openings - 25 Openings	None	N/A	0.04	
	Storage				
	- Contact Internal Roof Tank	None	N/A	4.0	1,400,000 gallons
	- Contact Internal Roof Tank	None	N/A	4.0	1,400,000 gallons
	- Fixed Roof Tank	None	N/A	3.6	3,700 gallons
	Loading/Handling - Ship Unloading	None	N/A	1.7	62 lb/hr CCl_4 emissions 60 hrs/yr
	Secondary - F-11/12 Waste Stream	PACT^R (Powdered Activated carbon treatment)	NR	0	No CCl_4 reported in this waste stream
Kaiser Aluminum/Gramercy, LA[5]	Equipment Leak	None	N/A	12.2	
	Equipment Openings				
	- 6 Scheduled Openings	None	N/A	0.8	
	- 4 Non-Scheduled Openings	None	N/A	0.5	
	- 16 Pump Openings	None	N/A	0.2	
	Storage				
	- Fixed Roof Tank	Refrigerated Scrubber	90	0.6	250,000 gallons
	- Pressure Recycle Tank	None	N/A	0	1,500 gallons
	- Pressure Return Tank	None	N/A	0	5,000 gallons
	Loading/Handling - Barges	None	N/A	1.1	25 Barges/yr at 100 lb/barge CCl_4 emissions
	Secondary - By-Product HCl	Neutralization	NR	0	

TABLE 4-3. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Penwalt/Calvert City, KY[6,7]	Process				
	- Recycle Tank Vent	None	N/A	0.2	
	- Air Separation Vent	None	N/A	0.1	
	Equipment Leak	None	N/A	16.3	
	Equipment Openings				
	- 3 Openings	None	N/A	9.5	Service Tanks
	Storage				
	- Fixed Roof Tank	Condenser	85	2.5	300,000 gallons
	- Fixed Roof Tank	In Design	85[c]	4.8[d]	42,000 gallons
	- Fixed Roof Tank	In Design	85[c]	4.8[d]	42,000 gallons
	- Pressure Tank	None	N/A	0	3,100 gallons
	- Pressure Tank	None	N/A	0	3,100 gallons
	- Pressure Tank	In Design	85[c]	3.7[d]	28,150 gallons
	Loading/Handling				
	- Barge or Tank Cars	None	N/A	0.04	
	Secondary				
	Waste Stream 1	None	N/A	0	NPDES discharge
Essex/Racon, Wichita, KS[8]	Process				
	- H.F. Recovery Vent (Unit I)	Packed Water Scrubber	88	8.7	
	- H.F. Recovery Vent (Unit II)	Packed Water Scrubber	88	5.0	
	Equipment Leak	None	N/A	8.0	
	Equipment Openings				
	- 19 Openings	None	N/A	0.05	
	Storage				
	- Fixed Roof Tank	None	N/A	1.5	Report only breathing losses
	Secondary				
	- Spent NaOH Solution	None	N/A	<0.01	Disposal handled by Vulcan Chemical Co.

N/A = Not Applicable
NR = Not Reported

[a] No breathing losses occur during plant operations because of continuous CCl_4 feed.

[b] The control system is planned and efficiencies estimated.

[c] Reported control efficiencies were obtained by calculations.

[d] Reported emissions based on no controls.

perform annual inspections of valves and flanges and visual inspections of pumps and compressors every 8 hours for leak detection. Currently, Allied has a daily visual inspection program. DuPont in Antioch, CA is under the regulations set by the Bay Area Air Quality Management District (BAAQMD). BAAQMD requires annual inspection of valves and flanges for leaks. DuPont's operators perform leak checks, but the frequency of the repair is unknown. Illinois prohibits Allied's plant in Danville from discharging more than 8 pounds of organic material per hour through equipment leaks unless controlled by a system with 85 percent efficiency. Pumps and compressors may not discharge over two cubic inches of liquid volatile organic material in any 15 minute period. Allied plant personnel perform daily visual inspections for leaks on all process components.

The State of Louisiana began requiring a VOC leak patrol/repair program in January 1984. This program has to be implemented by December 31, 1987. Requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and valves in liquid service, monthly leak detection for compressor seals and valves in gas service, and weekly visual inspection of pump seals. Repair or reasonable measures to minimize identified leaks is required within 15 days. Also, open-ended lines are required to be capped. Kaiser plant operators visually checked for leaks several times a shift in 1983 and also used a leak detector several times during a week. The frequency of repair was not reported.

The State of New Jersey does not specify inspection intervals or repair requirements at this time. The DuPont plant in Deepwater, N.J. currently makes periodic inspections for leaks, but at no set frequency. The frequency of repair was not reported.

The States of Michigan, Kentucky, and Kansas have no regulatory requirements for control of equipment leak CCl_4 emissions from CFC facilities. However, two facilities in these states do have their own control programs. Essex/Racon in Wichita, Kansas inspects all valves, flanges, pressure safety valves, pump seals, etc. on a monthly basis. Liquid leaks are detected visually and vapor leaks with a halocarbon detector. However, no repair program was mentioned in their response. DuPont in Montague, Michigan has trained their operators to look for and report leaks on a regular basis, but no time table or repair program was mentioned. Only Penwalt in Calvert City, Kentucky did not report a program for control of equipment leak emissions.

Carbon tetrachloride storage emissions from CFC production facilities range from 0 Mg/yr at Allied's plant in El Segundo, CA to 12.1 Mg/yr at the Pennwalt facility in Calvert City, KY. Storage emissions account for 24 percent of the total CFC industry emissions. State regulations impacting storage tank emissions are similar in many respects across the nation.

The Allied CFC plant in El Segundo, California met SCAQMD requirements by using a vapor recovery system. Greater than 98 percent control efficiency was reported for the system.

DuPont's facility in Antioch, CA, presently uncontrolled, must meet standards set by BAAQMD. To meet state standards, DuPont plans to upgrade their fixed roof tank with a low temperature condenser followed by a carbon adsorber. Calculated estimates provided by DuPont indicate that this system will provide greater than 98 percent control efficiency for the current CCl_4 emissions of 6.8 Mg/yr.[4]

Illinois regulations require all volatile organic storage tanks over 40,000 gallons to be pressure tanks or to be equipped with a floating roof, a vapor recovery system capable of 85 percent collection and a disposal system which prevents further emissions to the atmosphere, or equipment to provide equivalent control efficiency. Allied's plant in Danville has one fixed roof tank and reported no CCl_4 emissions. They contend that continuous withdrawal of CCl_4 from the storage tank for CFC production reduces or eliminates the potential for emissions.

DuPont's facility in Montague, MI must meet state regulations which require storage tanks over 40,000 gallons to be pressure tanks or have either a floating roof or a vapor recovery system with 90 percent control efficiency. DuPont controls its emissions by using a 0.4 psig conservation vent, a vapor recovery system, and by continuously feeding CCl_4 to the CFC process at volumes greater than the vapor expansion in the storage tanks.

Storage tank emissions at Essex/Racon in Wichita, Kansas and Penwalt in Calvert City, Kentucky are not regulated. Racon has one fixed roof tank with reported breathing losses of 1.5 Mg/yr. They report no working losses because CCl_4 is received via pipeline. Penwalt has 6 storage tanks (3 fixed roof and 3 pressure types) with a condenser on one of the fixed roof tanks providing 85 percent control of CCl_4 emissions.

In the State of Louisiana, VOC storage tanks over 40,000 gallons which are not pressure tanks must have a submerged fill pipe and one of the following:

(1) internal or external floating roof,

(2) a vapor loss control system equivalent to floating roof, or

(3) other equivalent equipment or means.

Kaiser Aluminum's 250,000 gallon fixed roof tank uses a refrigerated scrubber (90 percent efficiency) to meet these state regulations. In the State of Louisiana, smaller VOC storage tanks, 250 to 40,000 gallons, must have one of the following controls:

(1) submerged fill pipe,

(2) vapor recovery system, or

(3) other equivalent equipment or means.

Kaiser's two smaller tanks are pressure tanks and reportedly have minimal emissions.

New Jersey requires that CCl_4 storage tanks over 300,000 gallons be controlled with an external or internal floating roof and at least one tight seal. DuPont's facility in Deepwater has two 1,400,000 gallon storage tanks with contact internal floating roofs. It's third tank (3,700 gallons) is a fixed roof tank which has no emission controls.

Handling emissions range from 0 to 1.7 Mg/yr and account for approximately 2 percent of the total CFC industry emissions. State regulations governing handling emissions vary from none in Kansas and Kentucky to a limit of 8 pounds per hour in Illinois. Most states require at least minimal control by using submerge fill. Allied's facility in California uses a vapor recovery system to control loading emissions.

The State of Illinois has the following unloading regulations:

(1) Facilities unloading greater than 40,000 gallons per day into trucks or trailers must use submerged loading or equally effective control. Otherwise, emissions must be restricted to less than 8 pounds per hour.

(2) Unloading into stationary tanks over 250 gallons must be done with a permanent submerged loading pipe or equivalent, unless it is a pressure tank or a vapor recovery system.

The Allied plant in Illinois meets these regulations by using a vapor recovery system when unloading CCl_4. An estimated 0.18 Mg/yr of CCl_4 is emitted from the storage tank vent during the unloading operations.

Michigan regulations require that all unloading facilities handling over 5,000,000 gallons per year have:

(1) submerged unloading for facilities outside of an ozone nonattainment area,

(2) vapor recovery such that emissions are less than 0.7 pounds of organic vapor per 1,000 gallons of organic compound unloaded, in nonattainment areas.

The DuPont plant in Montague uses vapor balance when loading CCl_4 from rail cars to their storage tanks. The only emissions occur when the rail car is opened for sampling and connecting the liquid and vent lines.

As mentioned before, the States of Kansas and Kentucky have no regulations concerning loading emissions. Essex/Racon in Kansas receives CCl_4 shipments directly via a pipeline and has no unloading emissions. Penwalt (KY) pumps CCl_4 directly from either a barge or tank car to their storage tanks. They report CCl_4 handling emissions of 0.04 Mg/yr for 1983.

The State of Louisiana requires VOC loading facilities with daily throughput of 40,000 gallons or more to have vapor collection and disposal, or an equivalent control. Spill prevention for the filling equipment is also required. Barge and ships unloading are exempt from these requirements. Kaiser Aluminum has unloading emissions of 1.1 Mg/yr. Since they unload CCl_4 mostly from barges, they are exempt from State unloading regulations.

Transfer operations in New Jersey require submerged filling or equivalent control when transferring volatile organic substances into any vessel over 2,000 gallons (marine vessels exempted). DuPont's facility has CCl_4 emissions of 1.7 Mg/yr, but is exempt from state regulations because it receives shipments by ships.

Emissions from secondary sources, equipment openings, and relief devices are minimal at most facilities. Equipment opening emissions account for eight percent and secondary emissions account for less than 0.1 percent of the total emissions from CFC industry. None of the plants reported relief valve discharges in 1983. There are no State regulations for equipment openings or secondary emission sources.

4.3 COST OF ADDITIONAL CONTROLS

Cost estimates were developed for control of process, fugitive and storage emissions at each CFC facility where these emissions are presently not well controlled. A summary of the cost effectiveness to control these emission sources is presented in Table 4-4 and discussed in the following sections.

Table 4-5 summarizes the estimated CCl_4 emission reductions as a function of cost effectiveness. The emission reductions are shown by the emission types as well as the total for the entire CFC industry. A total potential emission reduction of 63.6 Mg (48 percent) is technically feasible.

4.3.1 Control of Process Vent Emissions

The cost of controlling CCl_4 process vent emissions by incineration was estimated for the two CFC facilities reporting process vent emissions. Carbon tetrachloride process emissions from Penwalt in Calvert City, Kentucky can be reduced by 0.2 Mg/yr at a cost of $63,800/Mg of VOC. At Essex/Racon in Wichita, Kansas CCl_4 emissions can be reduced 13.4 Mg/yr at a cost of $36,800/Mg of VOC.

TABLE 4-4. COSTS OF ADDITIONAL CONTROLS AT CFC PRODUCTION FACILITIES

Company/Location	Emission Type/Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/Yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Allied/ El Segundo, CA	Equipment Leak	Equipment & Work Practices	3.1/3.1	17.0	1.0	8.7	2,800	2,800
Allied/ Danville, IL	Equipment Leak	Equipment & Work Practices	3.9/3.9	16.0	1.3	9.4	2,400	2,400
E.I. duPont/ Montague, MI	Equipment Leak	Equipment & Work Practices	4.2/4.2	15.7	1.4	10.7	2,600	2,600
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	0.4/0.4	23.3	0.1	6.0	15,100	15,100
		Int. Floating Roof-SS	0.4/0.4	27.0	0.1	7.0	16,100	16,100
		Refrigerated Condenser	0.6/0.6	110.8	0.2	28.9	48,800	48,800
E.I. duPont/ Antioch, CA	Equipment Leak	Equipment & Work Practices	2.1/2.1	21.8	0.7	12.3	5,800	5,800
E.I. duPont/ Deepwater, NJ	Equipment Leak	Equipment & Work Practices	2.8/2.8	14.7	0.9	8.9	3,200	3,200
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	3.1/3.1	11.5	1.0	2.0	600	600
		Int. Floating Roof-SS	3.1/3.1	13.0	1.0	2.4	800	800
		Refrigerated Condenser	3.1/3.1	265.2	1.0	68.7	22,300	22,300
Kaiser Aluminum/ Gramercy, LA	Equipment Leak	Equipment & Work Practices	7.5/7.5	65.6	2.5	29.0	3,800	3,800
Penwalt/ Calvert City, KY	Process	Incineration	0.2/6.5	1,219.0	0	412.4	1,676,600	63,800
	Equipment Leak	Equipment & Work Practices	9.4/9.4	43.8	3.1	25.4	2,700	2,700
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	8.8/8.8	46.1	2.9	9.2	1,100	1,100
		Int. Floating Roof-SS	8.9/8.9	53.6	2.9	11.2	1,300	1,300
		Refrigerated Condenser	8.2/8.2	221.6	2.7	55.5	6,800	6,800
Essex/Racon Wichita, KS	Process	Incineration	13.4/13.4	1,219.0	0	492.9	36,800	36,800
	Equipment Leak	Equipment & Work Practices	3.5/3.5	66.7	1.1	24.7	7,100	7,100
	Storage - Fixed-Roof Tank	Int. Floating Roof-PO	1.2/1.2	15.3	0.4	3.6	3,000	3,000
		Int. Floating Roof-SS	1.2/1.2	17.5	0.4	4.2	3,400	3,400
		Refrigerated Condenser	1.3/1.3	110.8	0.4	28.7	22,000	22,200

TABLE 4-5. ESTIMATED CCl_4 EMISSION REDUCTIONS AS A FUNCTION OF COST EFFECTIVENESS

Cost Effectiveness ($/Mg of VOC) Range	Nationwide CCl_4 Emission Reduction (Mg/yr)			
	Process	Equipment Leak	Storage	Total
Credit	-	-	-	-
0 - 500	-	-	-	-
500 - 1,000	-	-	3.1	3.1
1,000 - 2,000	-	-	8.8	8.8
2,000 - 5,000	-	2.1	1.2	3.3
>5,000	13.6	34.4	0.4	48.4
TOTAL	13.6	36.5	13.5	63.6

4.3.2 Control of Equipment Leak Emissions

Equipment leak emissions totaling 69.9 Mg/yr account for a majority of the current estimated emissions from the CFC industry. As discussed in a previous section, several CFC facilities have inspection programs for detection of equipment leaks, but did not mention repair programs. For this reason, it was assumed that no equipment leak controls are in place. Therefore, costs were estimated for adding controls at all CFC facilities. The control techniques costed are those required under the benzene fugitives NESHAP. Costing methods are shown in Appendix C.

The estimated cost effectiveness for controlling equipment leak emissions at the CFC facilities ranges from $2,400/Mg of VOC to $7,100/Mg of VOC. Equipment leak carbon tetrachloride emissions could be reduced by 52 percent (36.5 Mg/yr) if additional controls were used at all CFC facilities.

4.3.3 Control of Storage Emissions

Cost estimates were developed for control of fixed-roof tanks emitting 33.3 Mg/yr of CCl_4. Three control options were evaluated: contact internal roof with a primary seal (FR-PO), contact internal roof with primary and secondary seals (FR-SS), and a refrigerated condenser.

The estimated cost effectiveness for controlling storage emissions at CFC facilities ranges from $600/Mg of VOC to over $48,800/Mg of VOC. The additional storage controls will reduce CCl_4 emissions from CFC facilities by 41 percent (13.5 Mg/yr).

4.4 REFERENCES

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2. Mannsville Chemical Products. Chemical Products Synopsis - Fluorocarbons. Cortland, New York. August 1982.

3. Letter and attachments from Cooper, J. E., Allied Corporation, to Farmer, J. R., EPA:ESED, January 25, 1985. Response to Section 114 Letter.

4. Letter and attachments from Coleman, J. B., E. I. DuPont De Nemours and Company, to Farmer, J. R., EPA:ESED, January 30, 1985. Response to Section 114 Letter.

5. Letter and attachments from Watts, R. H., Kaiser Aluminum and Chemical Corporation, to Farmer, J. R., EPA:ESED, March 11, 1985. Response to Section 114 Letter.

6. Letter and attachments from Schroeder, P. L., Penwalt Corporation, to Farmer, J. R., EPA:ESED, January 2, 1985. Response to Section 114 Letter.

7. Letter and attachments from Schroeder, P. L., Penwalt Corporation, to Farmer, J. R., EPA:ESED, February 19, 1985. Response to Section 114 Letter.

8. Letter and attachments from Turner, M. R., Racon, Inc., to Farmer, J. R., EPA:ESED, December 21, 1984. Response to Section 114 Letter.

5.0 ETHYLENE DICHLORIDE PRODUCTION

Carbon tetrachloride can be formed as a byproduct in the production of ethylene dichloride (EDC). The formation of carbon tetrachloride is reportedly associated with the oxychlorination of ethylene.[1,2] This process is used in combination with direct chlorination at the majority of ethylene dichloride facilities listed in Table 5-1. The total estimated CCl_4 emissions from the production of ethylene dichloride are 71 Mg/yr.

Although Section 114 letters were sent to all but one EDC producer, only two companies responded fully to the questionnaire. A number of the companies indicated no awareness of or reason to suspect CCl_4 emissions.

5.1 PROCESS DESCRIPTION

Ethylene dichloride is generally produced in the United States by direct chlorination of ethylene, oxychlorination of ethylene, or a combination of the two. The oxychlorination process is reportedly the source of CCl_4 formation, and is the process of interest in this chapter. The oxychlorination of ethylene is accomplished via the following reaction:

$$\underset{\text{(ethylene)}}{2\ H_2C=CH_2} + \underset{\text{(oxygen)}}{O_2} + \underset{\text{(hydrogen chloride)}}{4HCl} \longrightarrow \underset{\text{(EDC)}}{2ClCH_2CH_2Cl} + \underset{\text{(water)}}{2H_2O}$$

The reaction is normally carried out in the vapor phase is either a fixed-bed or fluid bed reactor.[1] Cupric chloride is the most common catalyst for this reaction. Typically, it takes place at 138 to 483 kPa gauge (20 to 70 psia) and 200° to 315°C (390° to 600°F).[3] Oxygen for this reaction may be supplied in the form of pure oxygen or air. Since HCl is required for the oxychlorination process, this process is typically used in combination with the manufacture of vinyl chloride monomer, a source of HCl byproduct.

TABLE 5-1. PRODUCERS OF ETHYLENE DICHLORIDE[4]

Company	Location	Production Capacity (Mg/Yr)
Atlantic Richfield Co.	Port Arthur, TX	227,000
Borden, Inc.	Geismar, LA	231,000
Diamond Shamrock	Deer Park, TX	86,000
Dow Chemical, U.S.A.	Freeport, TX	726,000
	Oyster Creek, TX	551,000
	Plaquemine, LA	936,000
Ethyl Corporation	Baton Rouge, LA	317,000
Formosa Platstics Corp., U.S.A.	Baton Rouge, LA	249,000
	Point Comfort, TX	385,000
Georgia Gulf	Plaquemine, LA	748,000
BF Goodrich Company	La Porte, TX	719,000
	Calvert City, KY	453,000
	Convent, LA	363,000
PPG Industries	Lake Charles, LA	1,220,000
Shell Oil Company	Deer Park, TX	635,000
Union Carbide Corporation	Taft, LA	68,000
	Texas City, TX	68,000
Vista Chemical	Lake Charles, LA	524,000
Vulcan Materials Company	Geismar, LA	159,000

Carbon tetrachloride may be formed as a byproduct in oxychlorination by the side reaction:

$$\underset{\text{(ethylene)}}{H_2C = CH_2} \quad + \quad \underset{\text{(oxygen)}}{3O_2} \quad + \quad \underset{\text{(hydrogen chloride)}}{8HCl} \longrightarrow \underset{\text{(Carbon tetrachloride)}}{2CCl_4} \quad + \quad \underset{\text{(water)}}{6H_2O}$$

This side reaction could cause the presence of CCl_4 in the product EDC and result in emissions of CCl_4.

5.2 CURRENT CONTROLS AND ESTIMATED EMISSIONS

Two facilities, Shell in Deer Park, Texas and Borden in Geismar, Louisiana, responded fully to the Section 114 request. These two facilities supplied estimates on process vent emissions, equipment count data, and storage tank data. Emission estimates for these sources are summarized in Table 5-2. Controls and estimated emissions for individual sources at these facilities are presented in Table 5-3. Georgia Gulf also provided storage tank data, but did not supply equipment count data or indicate process vent emissions. Georgia Gulf did indicate small quantities of CCl_4 in a number of process streams and provided data on destruction of liquid waste containing CCl_4. Vulcan/Geismar supplied information on one intermittent process vent only. The other companies responded that they were not aware of any CCl_4 emissions from their facilities. Since the oxychlorination process is generally common to all EDC plants, it is expected that similar CCl_4 emissions occur at other facilities. For the purpose of this study, emissions from other EDC facilities were estimated based on received data (from three companies) and using methods presented in the following discussion. The Source Assessment Document for Ethylene Dichloride Emissions was used to identify controls at each EDC facility except the Ethyl/Baton Rouge facility where the oxychlorination process is not used.[3] Estimated emissions and controls at all other EDC facilities are presented in Tables 5-2 and 5-3.

TABLE 5-2. SUMMARY OF ESTIMATED 1983 CCl_4 EMISSIONS FROM EDC PRODUCTION FACILITIES (Mg)

Company/Location	Process	Equipment Leak	Storage	Secondary	Total
Atlantic Richfield/Port Arthur, TX	1.2	1.0	0.005	0	2.2
Borden/Geismar, LA	0.006	0.51	0.00002	0	0.5
Diamond Shamrock/Deer Park, TX	0.46	1.0	0.14	0	1.6
Dow Chemical/Freeport, TX	3.9	1.0	0.44	0	5.3
Dow Chemical/Oyster Creek, TX	3.0	1.0	0.032	0	4.0
Dow Chemical/Plaquemine, LA	5.0	1.0	0.20	0	6.2
Formosa Plastics/Baton Rouge, LA	1.3	1.0	2.0	0	4.3
Formosa Plastics/Point Comfort, TX	2.1	1.0	0.055	0	3.2
Georgia Gulf/Plaquemine, LA	4.0	1.0	4×10^{-6}	5×10^{-6}	5.0
BF Goodrich/La Porte, TX	3.9	1.0	0	0	4.9
BF Goodrich/Calvert City, KY	2.4	1.0	7.3	0	10.7
BF Goodrich/Convent, LA	2.0	1.0	0	0	3.0
PPG Industries/Lake Charles, LA	6.5	1.0	0	0	7.5
Shell/Deer Park, TX	0.0015	1.5	0.00004	0.02	1.5
Union Carbide/Taft, LA	0.37	1.0	0.35	0	1.7
Union Carbide/Texas City, TX	0.37	1.0	0.35	0	1.7
Vista Chemical/Lake Charles, LA	2.8	1.0	0.52	0	4.3
Vulcan Materials/Geismar, LA	0.88	1.0	1.3	0	3.2
TOTAL	40.2	18.0	12.6	0.02	70.8

TABLE 5-3. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT EDC FACILITIES

Company/Location	Type of Emission Source	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Borden/Geismar, LA[2]	Process Vents	Incinerator	98[a]	0.006	
	Equipment Leak	None	0	0.51	
	Storage				
	- Fixed Roof Tank	Incinerator	98[a]	0.00002	50,000 gallons, 5% CCl_4
Shell Chemical/Deer Park, TX[5]	Process Vents	Incinerator	98[a]	0.0015	
	Equipment Leak	None	0	1.48	
	Storage				
	- Fixed Roof Tank	Incinerator	98[a]	1.3×10^{-5}	376,000 gallons, 0.1% CCl_4
	- Fixed Roof Tank	Incinerator	98[a]	1.3×10^{-6}	
	- Fixed Roof Tank	Incinerator	98[a]	8.9×10^{-6}	
	- Fixed Roof Tank	Incinerator	98[a]	8.9×10^{-6}	
	- Fixed Roof Tank	Incinerator	98[a]	2.0×10^{-6}	282,000 gallons, 0.1% CCl_4
	- Fixed Roof Tank	Incinerator	98[a]	1.1×10^{-6}	424,000 gallons, 0.1% CCl_4
	Secondary	Incinerator	98[a]	0.02	
Georgia Gulf/Plaquemine, LA[6]	Process Vents	Incinerator	98	4.0[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	*	*	1.0×10^{-6}	
	- Fixed Roof Tank	*	*	1.0×10^{-6}	
	- Fixed Roof Tank	*	*	1.0×10^{-6}	
	- Fixed Roof Tank	*	*	1.0×10^{-6}	
	Secondary	Incinerator	98[a]	5.1×10^{-6}	
Atlantic Richfield/ Port Arthur, TX	Process Vents	Incinerator	98	1.2[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- *	*	*	0.005[c]	
Diamond Shamrock/Deer Park, TX	Process Vents	Incinerator	98	0.46[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	Incinerator	98	0.14[c]	

TABLE 5-3. (Continued)

Company/Location	Type of Emission Source	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Dow Chemical/Freeport, TX	Process Vents	Incinerator	98	3.9[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	Vent Condenser	87	0.15[c]	170,000 gallon
	- Fixed Roof Tank	Vent Condenser	37	0.016[c]	210,000 gallon
	- Fixed Roof Tank	Vent Condenser	37	0.016[c]	210,000 gallon
	- Fixed Roof Tank	Vent Condenser	67	0.020[c]	127,000 gallon
	- Fixed Roof Tank	Vent Condenser	93	0.12[c]	2,683,000 gallon
	- Fixed Roof Tank	Vent Condenser	93	0.12[c]	2,683,000 gallon
Dow Chemical/Oyster Creek, TX	Process Vents	Incinerator	98	3.0[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	Refrigerated Condenser	98[a]	0.011[c]	436,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	98[a]	0.011[c]	436,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	98[a]	0.006[c]	185,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	98[a]	0.004[c]	436,000 gallon
Dow Chemical/Plaquemine, LA	Process Vents	Incinerator	98	5.0[b]	
	Equipment Leak	None		1.0[b]	
	Storage				
	- Fixed Roof Tank	Refrigerated Condenser	95	0.006[c]	124,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.020[c]	44,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.008[c]	34,600 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.020[c]	905,800 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.050[c]	438,600 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.052[c]	1,192,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	95	0.045[c]	243,000 gallon
Formosa Plastics/Baton Rouge, LA	Process Vents	Incinerator	98	1.3[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	Vapor Recovery	85	0.72[c]	2,540,000 gallon
	- Fixed Roof Tank	Vapor Recovery	85	0.72[c]	2,540,000 gallon
	- Fixed Roof Tank	Conserv. Vent & Inerts	80	0.50[c]	345,000 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.008[c]	730,000 gallon
	- Fixed Roof Tank	None	0	0.05[c]	55,000 gallon

TABLE 5-3. (Continued)

Company/Location	Type of Emission Source	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Formosa Plastics/ Point Comfort, TX	Process Vents	Incinerator	98	2.1[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	Incineration	98[a]	0.002[c]	529,000 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.006[c]	529,000 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.020[c]	529,000 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.025[c]	2,645,000 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.001[c]	211,600 gallon
	- Fixed Roof Tank	Incineration	98[a]	0.001[c]	211,600 gallon
BF Goodrich/LaPorte, TX	Process Vents	Incinerator	98	3.9[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- *	*	*	0	
BF Goodrich/Calvert City, KY	Process Vents	Incinerator	98	2.4[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- *	*	*	0.30[c]	
	- *	*	*	2.5[c]	
	- *	*	*	1.4[c]	
	- *	*	*	0.1[c]	
	- *	*	*	0.05[c]	
	- *	*	*	0.018[c]	
	- *	*	*	0.05[c]	
	- *	*	*	0.010[c]	
	- *	*	*	0.030[c]	
	- *	*	*	0.024[c]	
	- *	*	*	1.6[c]	
	- *	*	*	1.2[c]	
	- *	*	*	0.025[c]	
BF Goodrich/Convent, LA	Process Vents	Incinerator	98	2.0[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- *	*	*	0	

TABLE 5-3. (Continued)

Company/Location	Type of Emission Source	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
PPG Industries/Lake Charles, LA	Process Vents	Incinerator	98	6.5[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- 8 Fixed Roof Tanks	Incineration	98[a]	0[c]	
	- 3 Fixed Roof Tanks	Refrigeration/Recycle	98[a]	0[c]	
Union Carbide/Taft, LA	Process Vents	Incinerator	98	0.37[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof tank	Refrigeration	68	0.35[c]	
Union Carbide/Texas City, TX	Process Vents	Incinerator	98	0.37[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage[d]				
	- Fixed Roof Tank	Refrigeration	68	0.35	
Vista Chemical/Lake Charles, LA	Process Vents	Incinerator	98	2.8[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- *	*	*	0.52[c]	
	- *	*	*	0[c]	
	- *	*	*	0.0002	
	- *	*	*	0[c]	
	- *	*	*	0[c]	
	- *	*	*	0.0002[c]	
	- *	*	*	0[c]	
	- *	*	*	0[c]	
Vulcan Materials/Geismar, LA[7]	Process Vents				
	- Acid Scrubber Vent	None	0	0.018	Intermittent
	- Other Vents	Incinerator	98	0.086[b]	
	Equipment Leak	None	0	1.0[b]	
	Storage				
	- Fixed Roof Tank	None	0	0.20[c]	7,060 gallon
	- Fixed Roof Tank	None	0	0.24[c]	2,300 gallon

TABLE 5-3. (Continued)

Company/Location	Type of Emission Source	Present Controls	Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Vulcan Materials/Geismar, LA[7] (Continued)	- Fixed Roof Tank	None	0	0.082[c]	34,000 gallon
	- Fixed Roof Tank	None	0	0.082[c]	34,000 gallon
	- Fixed Roof Tank	None	0	0.082[c]	34,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	90	0.18[c]	79,500 gallon
	- Fixed Roof Tank	Refrigerated Condenser	90	0.088[c]	1,000,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	90	0.090[c]	1,000,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	90	0.090[c]	1,000,000 gallon
	- Fixed Roof Tank	Refrigerated Condenser	90	0.19[c]	1,700,000 gallon

* = Confidential

[a] Control efficiency reported by company is greater than 98 percent.

[b] Estimate based on information provided by Borden and Shell.

[c] Estimate based on information available in Source Assessment of Ethylene Dichloride Emissions and estimated CCl_4 is 2.5 of VOC.

[d] No information available. Estimated to be the same as the Taft, Louisiana facility.

Process vent emission estimates for the Borden and Shell facilities were obtained directly from their Section 114 responses. Borden reported uncontrolled process vent emissions of 60.0 Mg/yr and Shell reported uncontrolled emissions of 14.8 Mg/yr. These emissions are controlled greater than 98 percent at both facilities by incineration. Section 114 responses for the Shell and Borden facilities indicate that CCl_4 emissions are from the light ends column vent in the EDC purification section of the process. This vent is controlled at all EDC production facilities by thermal oxidation.[3]

Using the published capacity for the Shell facility and one half of the published capacity for the Borden facility presented in Table 5-1, an average uncontrolled process vent emission factor of 0.27 Kg CCl_4/Mg EDC production was calculated. Only one half of the Borden capacity was used because approximately half of the Borden capacity is accounted for by the acetylene process which has no CCl_4 emissions. The uncontrolled emission factor was multiplied by the published capacity for each of the other facilities to obtain estimated uncontrolled emissions. Since thermal oxidation with greater than 98 percent destruction is used to control all purification section process vents in EDC production facilities, uncontrolled emissions estimates were multiplied by 0.02 (98 percent control) to estimate current emissions. These estimates are presented in Table 5-3. Estimated process vent emissions total 40 Mg/yr for all EDC facilities accounting for 57 percent of total estimated emissions from EDC facilities.

The B.F. Goodrich facility in Calvert City, Kentucky has one uncontrolled process vent. All process vents, except the oxychlorination vent, are controlled by incineration at this facility. Information from the Shell and Borden responses indicate that CCl_4 emissions are from the light ends column rather than the oxychlorination vent. Therefore, this study assures that there were no CCl_4 emissions from this vent. However, it is possible that some CCl_4 may be emitted from the oxychlorination vent. Previous studies done for EPA have estimated CCl_4 emissions as high as 35 Mg/yr for this vent at the B.F. Goodrich facility.[8]

The relatively high degree of control for process vents at EDC plants is the result of the vinyl chloride NESHAP requiring control of process vent streams (except the oxychlorination vent) to less than 10 ppm vinyl chloride.[9] Since practically all vent streams from EDC processes contain some vinyl chloride, all process vent streams are typically incinerated to meet regulatory requirements. The uncontrolled vent reported by Vulcan does not contain vinyl chloride. The oxychlorination vent is subject to a separate standard, 0.2 gram of vinyl chloride/kilogram of EDC production. Incineration is used to meet this requirement at all facilities except BF Goodrich in Calvert City, Kentucky.

The estimated equipment leak CCl_4 emissions from all EDC production facilities total 18 Mg/yr, accounting for 25 percent of all EDC emissions. Only two facilities, Borden and Shell, provided information sufficient to estimate equipment leak emissions. Estimated equipment leak emissions for these two facilities are presented in Table 5-3. Equipment leak emissions are not a function of production, but a function of plant complexity. Since the complexity of individual facilities is unknown, equipment leak emissions for all other facilities are assumed to be the average for the Borden and Shell facilities (1 Mg/yr).

All EDC production facilities are required to have equipment leak control programs for vinyl chloride under the vinyl chloride NESHAP. These programs are to be devised by each facility and approved by the Administrator. Therefore, the equipment leak control programs vary from plant to plant. Recently proposed revisions to the existing vinyl chloride NESHAP will require programs consistent with those required by the benzene fugitives NESHAP. Although these programs are for vinyl chloride equipment leaks, it is likely that many of the pieces of equipment in carbon tetrachloride service are also in vinyl chloride service. Therefore, effective control of vinyl chloride equipment leak emissions probably results in at least some control of carbon tetrachloride equipment leak emissions. However, with the available data, it is not possible to quantitatively assess the control level and no credit is given in equipment leak emission estimates. Other regulations that will affect carbon tetrachloride equipment leak emissions are equipment leak VOC regulations recently enacted in Louisiana (state wide) and Texas (Harris Co.).[10,11] These regulations require annual leak detection and repair for pump seals and valves in liquid service, monthly leak detection and repair for compressor seals and valves in gas service, weekly visual inspection of pump seals, and capping of open ended lines. The final compliance date for both Texas and Louisiana regulations is December 31, 1987.

Estimated storage emissions total about 13 Mg/yr for all facilities, accounting for 18 percent of EDC facility emissions. Three facilities, Borden, Shell, and Georgia Gulf provided data on storage tanks. Estimated storage emissions for these three facilities are presented in Table 5-3. Borden reported a storage tank containing several chlorinated compounds with five percent CCl_4 while Shell reported less than 0.15 percent CCl_4 in the product EDC. Based on 2.5 percent CCl_4 (the average) in the storage tanks, storage emissions were estimated for all other facilities. Since CCl_4 and EDC have similar vapor pressures, the CCl_4 emissions were estimated as 2.5 percent of VOC emissions for EDC storage tanks. The estimates for VOC emissions for EDC storage tanks were obtained from the Source Assessment of Ethylene Dichloride Emissions.[3] These estimates are presented in Table 5-3 along with present controls.

A number of EDC storage tanks are presently controlled by incineration or vapor recovery to meet requirements of the vinyl chloride NESHAP. There are also VOC storage tank regulations in Texas and Louisiana which are applicable. In Texas, storage tanks larger than 25,000 gallons must be controlled by an internal floating roof, an external floating roof (primary and secondary seal), or vapor recovery. In Louisiana, storage tanks larger than 40,000 must meet the same requirements.

The only other emission source reported was from the destruction of a liquid waste stream at the Shell and Georgia Gulf facilities. These emissions are estimated to be about 0.02 Mg/yr.

5.3 COSTS OF ADDITIONAL CONTROLS

Cost estimates were developed for control of process vent, equipment leak, and storage emissions that are not already well controlled. These estimates are presented in Table 5-4. The emission reductions that can be achieved by additional controls for different cost effective ranges are presented in Table 5-5. Methods used for estimating costs/cost effectiveness are presented in Appendix C.

5.3.1 Control of Process Vent Emissions

The costs of controlling the CCl_4 emitting process vent at Vulcan/Geismar by incineration were estimated. These costs are presented in Table 5-4. Carbon tetrachloride emissions from this vent can be reduced by 0.02 Mg at a cost effectiveness of $22,800,000/Mg of CCl_4 and $16,500/Mg of VOC.

5.3.2 Control of Fugitive Emissions

None of the facilities presently have equipment leak control programs specifically for CCl_4. It is not known if any of the equipment in CCl_4 service are affected by the vinyl chloride NESHAP. Therefore, equipment leak emission control techniques consistent with those required by the benzene equipment leak NESHAP were costed for the Shell and Borden facilities that supplied equipment count data. The estimated cost effectiveness of controlling equipment leak emissions at these two facilities are $230/Mg of VOC and $1,900/Mg of VOC for Shell and Borden, respectively. The costs and achievable emission reduction of equipment leak controls at other EDC facilities was estimated to be the average for the Shell and Borden facilities. Using the average net annual cost and average emission reduction, cost effectiveness for other facilities is estimated to be $260/Mg of VOC.

5.3.3 Control of Storage Emissions

Costs of controlling storage tank emissions were estimated for each tank not controlled 93 percent or better. Two options were costed: floating roof tanks with primary seals and floating roof tanks with primary and secondary seals. These cost estimates are presented in Table 5-4. The cost effectiveness of these controls range from -$280/Mg of VOC to $16,600/Mg of VOC.

TABLE 5-4. COSTS OF ADDITIONAL CONTROLS FOR EDC PRODUCTION FACILITIES

Company Location	Emission Source	Applicable Additional Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness $/Mg	
							CCl_4	VOC
Atlantic Richfield/ Port Arthur, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Borden/Geismar, LA	Equipment Leak	Equipment & Work Practices	0.3/4.3	16.7	1.4	8.1	25,300	1,900
Diamond Shamrock/Deer Park, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Dow Chemical/Freeport, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
	- Fixed Roof Tank	Floating Roof - PO Floating Roof - SS	0.1/5.0 0.1/5.8	34.0 40.0	1.8 1.9	7.1 8.6	52,000 60,000	1,300 1,300
	- 2 Fixed Roof Tanks	Floating Roof - PO Floating Roof - SS	0.015/0.60 0.015/0.61	33.6 39.1	0.2 0.2	8.6 10.1	572,000 664,000	14,300 16,600
	- Fixed Roof Tank	Floating Roof - PO Floating Roof - SS	0.02/0.75 0.02/0.78	33.0 39.0	0.25 0.25	11.3 10.0	420,000 512,000	10,500 12,800
	- 2 Fixed Roof Tanks	Floating Roof - PO Floating Roof - SS	0.1/4.0 0.1/4.5	125.1 149.1	1.4 1.5	31.5 37.7	292,000 336,000	7,300 8,400
Dow Chemical/Oyster Creek, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Dow Chemical/Plaquemine, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Formosa Plastics/ Baton Rouge, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
	- 2 Fixed Roof Tanks	Floating Roof - PO Floating Roof - SS	0.7/28.0 0.7/28.5	110.5 129.9	9.0 9.3	20.0 24.8	28,000 34,800	700 870
	- Fixed Roof Tank	Floating Roof - PO Floating Roof - SS	0.4/18.0 0.5/19.0	42.8 44.9	6.0 6.2	5.2 6.9	12,000 14,400	300 360
	- Fixed Roof Tank	Floating Roof - PO Floating Roof - SS	0.04/1.9 0.04/1.9	22.6 26.5	0.62 0.60	5.3 6.4	112,000 160,000	2,800 3,400
Georgia Gulf/Plaquemine, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260

TABLE 5-4. (Continued)

Company Location	Emission Source	Applicable Additional Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness $/Mg	
							CCl_4	VOC
BF Goodrich/Freeport, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
BF Goodrich/Calvert City, KY	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
			0.3/11.0	10.9	3.6	-0.7	-2,600	-65
			0.3/11.6	12.1	3.8	-0.6	-2,000	-50
			2.4/94.0	77.5	30.6	-10.2	-4,400	-110
			2.4/97.0	91.9	31.6	-6.1	-2,400	-60
			1.4/54.0	53.7	17.6	-3.5	-2,600	-65
			1.4/55.0	56.5	18.0	-1.5	-1,200	-30
			0.1/4.0	15.6	1.3	2.8	28,000	700
			0.1/4.0	17.7	1.3	3.4	34,800	870
			0.02/0.7	14.6	0.23	3.6	204,000	5,100
			0.02/0.7	16.9	0.23	4.5	256,000	6,400
			1.5/60.0	10.2	19.6	-16.9	-11,200	-280
			1.6/62.0	11.5	20.2	-17.2	-11,200	-280
			1.1/44.0	67.1	14.2	3.4	3,200	80
			1.1/45.0	78.1	14.7	5.8	5,200	130
BF Goodrich/Convent, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
PPG Industries/ Lake Charles, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Shell Chemical/Deer Park, TX	Equipment Leak	Equipment & Work Practices	1.0/197.7	210.6	65.2	45.3	45,300	229
Union Carbide/Taft, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
		Floating Roof - PO	0.3/13.0	94.9	4.3	20.6	64,000	1,600
		Floating Roof - SS	0.3/13.0	113.3	4.4	25.4	76,000	1,900

TABLE 5-4. (Continued)

Company Location	Emission Source	Applicable Additional Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness $/Mg	
							CCl_4	VOC
Union Carbide/Texas City, TX	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
		Floating Roof - PO	0.3/13.0	94.9	4.3	20.6	64,000	1,600
		Floating Roof - SS	0.3/13.0	113.3	4.4	25.4	76,000	1,900
Vista Chemical/ Lake Charles, LA	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
Vulcan Materials/Geismar, LA	Process Vent	Incinerator	0.02/24.2	1182.0	0	401.5	22,800,000	16,500
	Equipment Leak	Equipment & Work Practices	0.65/101.0	113.6	33.3	26.7	41,000	260
	Storage							
	- Fixed Roof Tank	Floating Roof - PO	0.2/7.5	13.3	2.5	1.0	5,600	140
		Floating Roof - SS	0.2/7.8	15.1	2.5	1.4	7,200	180
	- Fixed Roof Tank	Floating Roof - PO	0.2/9.0	10.6	2.9	-0.1	-400	-10
		Floating Roof - SS	0.2/9.2	11.9	3.0	0.13	600	15
	- 3 Fixed Roof Tanks	Floating Roof - PO	0.1/3.0	21.9	1.0	4.7	64,000	1,600
		Floating Roof - SS	0.1/3.2	25.7	1.0	5.8	72,000	1,800
	- Fixed Roof Tank	Floating Roof - PO	0.2/6.4	28.9	2.1	5.5	34,400	860
		Floating Roof - SS	0.2/6.8	33.7	2.2	6.7	40,000	1,000
	- Fixed Roof Tank	Floating Roof - PO	0.1/3.3	101.1	1.1	25.5	304,000	7,600
		Floating Roof - SS	0.1/3.4	121.1	1.1	30.7	360,000	9,000
	- 2 Fixed Roof Tanks	Floating Roof - PO	0.1/3.4	103.8	1.1	26.2	308,000	7,700
		Floating Roof - SS	0.1/3.5	124.4	1.1	31.6	360,000	9,000
	- Fixed Roof Tank	Floating Roof - PO	0.2/7.0	113.0	2.3	27.4	156,000	3,900
		Floating Roof - SS	0.2/7.3	135.0	2.4	33.1	180,000	4,500

PO - Primary seal only.
SS - Primary and secondary seals.

TABLE 5-5. ACHIEVABLE CCl_4 EMISSION REDUCTION FOR EDC PRODUCTION FACILITIES

	Nationwide CCl_4 Emission Reduction, Mg/Yr			
Cost Effectiveness Range, $/Mg of VOC	Process Vent	Fugitive	Storage[a]	Total
Credit	-	-	5.8	5.8
0 - 500	-	10.1	1.7	11.8
500 - 1,000	-	-	1.0	1.0
1,000 - 2,000	-	0.3	0.5	0.8
2,000 - 5,000	-	-	0.2	0.2
>5,000	0.02	-	0.4	0.42
TOTAL	0.02	10.4	9.6	20.0

[a] Emission reductions shown are for the most cost effective option.

5.4 REFERENCES

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6.0 CHLORINE PRODUCTION

Carbon tetrachloride (CCl_4) is used by several chlorine producers mainly as a scrubbing liquid to recover chlorine from a tail gas or inert gas vent stream following liquefaction. Another use of CCl_4 is as a diluent for nitrogen trichloride (NCl_3) which is often formed in chlorine production. In 1983, approximately 1,400 Mg of CCl_4 were used in chlorine production. Of this, about 990 Mg of CCl_4 were used for tail gas scrubbing and about 410 Mg of CCl_4 were used as a diluent for NCl_3. Use of CCl_4 in chlorine production accounts for about 0.5 percent of the total 1983 use of CCl_4 in the United States. Each of the two uses of CCl_4 in chlorine production will be discussed separately in the following sections.

6.1 TAIL GAS SCRUBBING

Three chlorine producers presently use CCl_4 for recovery of chlorine from tail gas at a total of seven facilities. Five of these facilities are owned by Diamond Shamrock. Vulcan Materials and E.I. duPont own the other two. All of these facilities use a technology licensed by Diamond Shamrock.

6.1.1 Process Description

A flow diagram for the tail gas scrubbing system is presented in Figure 6-1. Following compression and condensation operations in the liquefaction of chlorine, there are small quantities of noncondensible gases often referred to as the inert or tail gas stream. This stream also contains relatively small quantities of chlorine gas. At facilities using the tail gas scrubbing system, this stream is sent to a scrubber which uses CCl_4 as the scrubbing liquid. The chlorine is first absorbed in the liquid CCl_4. The chlorine/ CCl_4 mixture is then separated. The CCl_4 is recycled back to the absorber and the recovered chlorine is liquefied to be sold as product. Carbon tetrachloride vent emissions result from the contact of air and other gases with liquid CCl_4 in the scrubber. The vented gas stream contains about 0.5 percent CCl_4.

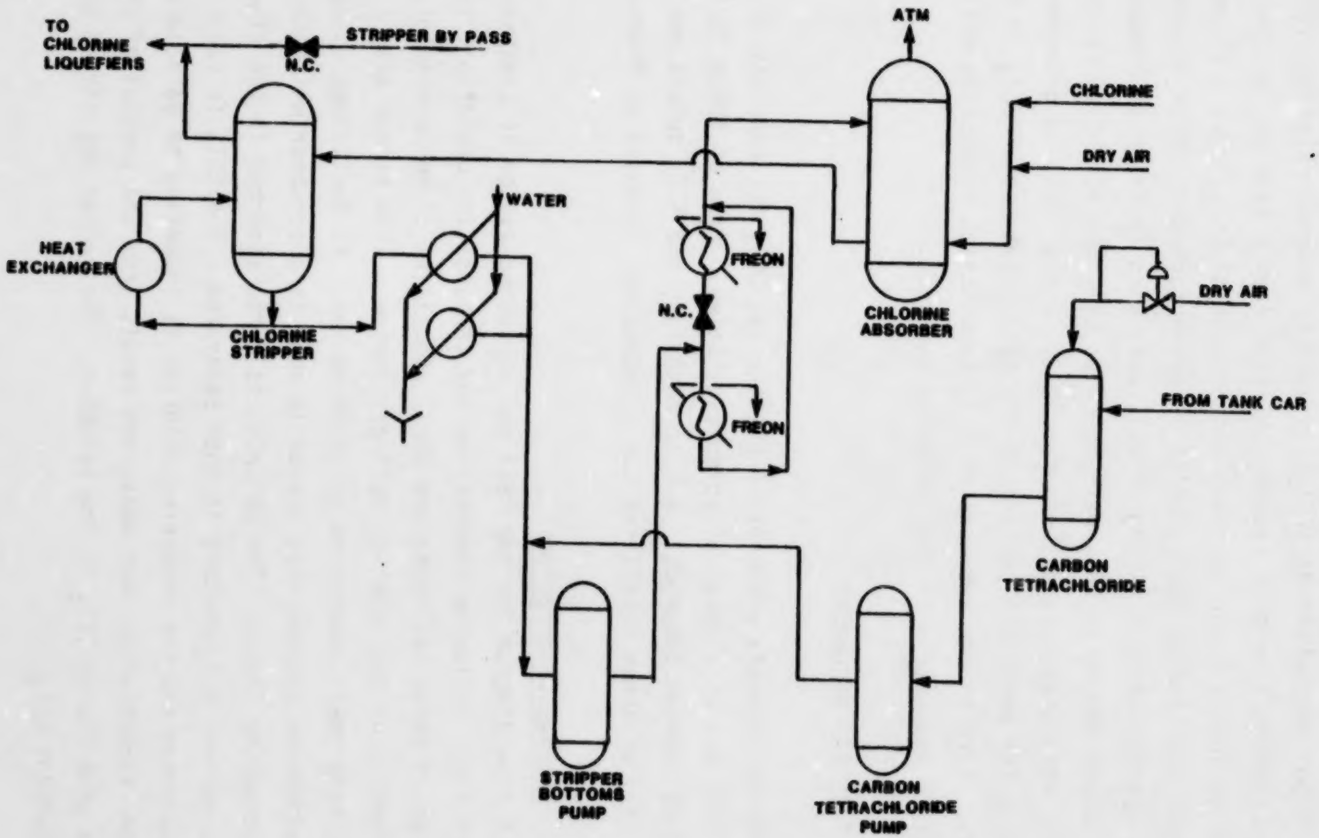
TO CHLORINE LIQUEFIERS
STRIPPER BY PASS
N.C.
ATM
CHLORINE
DRY AIR
WATER
HEAT EXCHANGER
FREON
N.C.
FREON
CHLORINE ABSORBER
DRY AIR
CHLORINE STRIPPER
FROM TANK CAR
CARBON TETRACHLORIDE
STRIPPER BOTTOMS PUMP
CARBON TETRACHLORIDE PUMP

Figure 6-1. Tail gas scrubbing with carbon tetrachloride.

6.1.2 Current Controls and Emissions

The major source of emissions from the use of CCl_4 for tail gas scrubbing is the absorber process vent. Emissions from this source total an estimated 292 Mg/yr for the seven facilities. Other reported emission sources are fugitive (equipment leaks), equipment opening losses, relief device discharges, and handling emissions. Total CCl_4 emissions from these sources is estimated to be 64 Mg/yr. A summary of emissions by facility and source is presented in Table 6-1. Emissions and controls for individual sources are presented in Table 6-2.

All seven facilities reported process vent emissions. As mentioned above, process vent emissions account for the majority of total emissions (82 percent). Process vent emissions are presently controlled by carbon adsorption at three facilities. Diamond Shamrock in Battleground, Texas, reported greater than 98 percent control efficiency and Vulcan in Geismar, Louisiana, reported greater than 90 percent control. E.I. duPont also employs a carbon adsorber, but the uncontrolled emissions and control efficiency are unknown.[1] Based on Diamond Shamrock and Vulcan responses, control efficiency of the carbon adsorber at E.I. duPont in Corpus Christi, Texas is estimated to be 95 percent. From information supplied by these two companies and published chlorine capacities, an uncontrolled emission factor of 550 kg of CCl_4 emitted per gigagram (Gg) of chlorine production capacity was calculated.[2] This factor was multiplied by the estimated production capacity of the DuPont facility, 297 Gg/yr, to estimate uncontrolled emissions.

One of the facilities, Vulcan in Geismar, is subject to process vent requirements in Louisiana. The State of Louisiana requires control of process vent emissions by incineration, carbon adsorption, or refrigeration. Process emissions at this facility are currently controlled by a carbon adsorber. The Diamond Shamrock facility in Battleground, Texas and the DuPont facility in Corpus Christi, Texas are also subject to State requirements. The State of Texas requires control of process vents emitting greater than 250 lbs/day in Harris and Neuces Counties. Both facilities are presently meeting this requirement by controlling process vent emissions with a carbon adsorber. Other facilities are not affected by any regulatory requirements for process vents.

TABLE 6-1. SUMMARY OF ESTIMATED 1983 EMISSIONS FROM CHLORINE PRODUCTION FACILITIES (Mg)

Company/Location	Process	Fugitive	Storage	Handling	Relief Device	Equipment Opening	Secondary	Total
Diamond Shamrock/ Deer Park, TX	100.0	3.8	0.04	-	-	0.2	-	104.0
Diamond Shamrock/ Delaware City, DE	89.8	8.2	0.17	-	0.4	0.15	-	98.7
Diamond Shamrock/ Battleground, TX	3.8	24.4	0.51	0.28	0.01	0.06	-	29.1
Diamond Shamrock/ Mobile, AL	32.4	3.7	-	0.03	-	0.01	-	36.1
Diamond Shamrock/ Muscle Shoals, AL	51.6	6.5	0.56	0.12	0.02	0.13	-	58.9
E.I. DuPont/ Corpus Christi, TX	8.2	7.1	-	-	-	-	-	15.3
Vulcan/ Geismar, LA	5.9	7.1	0.1	-	-	-	-	13.1
TOTAL	291.7	60.8	1.4	0.4	0.4	0.5	-	355.2

TABLE 6-2. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT FACILITIES PRODUCING CHLORINE

Company/Location	Type of Emission Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/yr)	Comments
Diamond Shamrock/Deer Park, TX[3]	Process Vents - Absorber Vent	None	0	100.0	Continuous Vent
	Equipment Leak	None	0	3.8	
	Equip. Openings	None	0	0.2	10 pump openings to replace seals
	Storage - Pressure Tank	None	N/R	0.04	Working losses only
Diamond Shamrock/Delaware City, DE[3]	Process Vents - Absorber Vent	None	0	89.8	Continuous Vent
	Relief Device	None	0	0.4	8 releases
	Equipment Leak	None	0	8.2	
	Equip. Openings	None	0	0.15	51 openings
	Storage - Fixed Roof Tank	None	0	0.17	9,400 gallon
Diamond Shamrock/Battleground, TX[3]	Process Vents - Absorber Vent	Carbon Adsorber	98[a]	3.8	Continuous vent
	Relief Device	None	0	<0.01	1 release
	Equipment Leak	None	0	24.4	
	Equip. Openings	None	0	0.06	4 openings
	Storage - Fixed Roof Tank	None	0	0.51	13,150 gallon
	Handling				
	- Ton Cylinders	None	0	0.241	
	- Dillution Pots	None	0	0.019	
	- Gunk Tanks	None	0	0.016	
Diamond Shamrock/Mobile, AL[3]	Process Vents - Absorber Vent	None	0	32.4	Continuous vent
	Equipment Leak	None	0	3.7	
	Equip. Openings	None	0	0.01	6 openings
	Handling	None	0	0.03	

TABLE 6-2. (Continued)

Company/Location	Type of Emission Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/yr)	Comments
Diamond Shamrock/Muscle Shoals, AL[3]	Process Vents - Absorber Vent	None	0	51.6	Continuous vent
	Relief Device	None	0	0.02	
	Equipment Leak	None	0	6.5	
	Equip. Openings	None	0	0.13	11 openings
	Storage - Fixed Roof Tank	None	0	0.56	7,470 gallon
	Handling	None	0	0.12	
E.I. DuPont/Corpus Christi, TX[1]	Process Vents - Absorber Vent	Carbon Adsorber	95[b]	8.2[b]	
	Equipment Leak	None	0	7.1[b]	
Vulcan Materials/Geismar, LA[4]	Process Vents - Absorber Vent	Carbon Adsorber	>90	5.9	
	Equipment Leak	None	0	7.1[b]	
	Storage - *	None	0	0.1	

* - Confidential information.
N/R - Not reported.

[a] Company reported greater than 98 percent control, but only 98 percent control efficiency is accepted without test data.

[b] Estimate based on Diamond Shamrock and Vulcan responses.

Equipment leaks are the second largest emission source, accounting for 17 percent (61 Mg) of estimated annual emissions. Equipment leak emissions were estimated for five of the facilities based on company supplied equipment count data. Equipment leak emissions for the remaining two facilities were estimated as the average of estimated equipment leak emissions at all Diamond Shamrock facilities except Battleground, Texas. The Battleground facility appears to be more complex than other facilities and may not be representative. Currently, none of the seven facilities have practices or controls to significantly reduce equipment leak emissions. Several of the facilities did report rupture discs under safety relief valves and estimated emissions reflect this.

Three of the seven facilities will likely be affected by recent equipment leak regulations enacted by Texas and Louisiana. Texas has enacted regulations for Harris County and Louisiana has enacted regulations statewide. One of the facilities in Texas, Diamond Shamrock in Battleground, is located in Harris County. The Texas and Louisiana regulations will require annual leak detection for pump seals and liquid valves, monthly leak detection for compressor seals and gas valves, and weekly visual inspection of pump seals. Reasonable attempts to repair leaks are required within 15 days. Also, open-ended lines are required to be capped.

Emissions from the remaining sources are relatively small accounting for less than 3 Mg or about 1 percent of total estimated emissions. Storage emissions account for 1.4 Mg of annual emissions, relief device discharges account for 0.4 Mg of annual emissions, equipment openings account for 0.5 Mg of annual emissions, and handling operations account for 0.4 Mg of annual CCl_4 emissions.

6.1.3 Cost of Additional Controls

Additional controls were evaluated for control of process vent, equipment leak, and storage emissions not already controlled at each facility. The estimated costs for controlling process vent and equipment leak emissions are presented in Table 6-3. The emission reduction achievable by control of these emissions is presented in Table 6-4 for different VOC cost-effectiveness

TABLE 6-3. COST OF ADDITIONAL CONTROLS FOR CHLORINE PRODUCTION FACILITIES

Company/Location	Emission Source	Applicable Additional Controls	CCl_4/VOC Emission Reduction (Mg/Yr)	Capital Cost (M/$)	Recovery Credit (M/$)	Net Annual Cost (M/$)	Cost Effectiveness $/Mg CCl_4	Cost Effectiveness $/Mg VOC
Diamond Shamrock/ Deer Park, TX	Process Vent	Incinerator Carbon Adsorber	98.1/98.1 95.0/95.0	1,209.0 140.3	0 31.4	420.9 16.4	4,300 170	4,300 170
	Equipment Leak	Equipment & Work Practices	1.6/1.6	12.7	0.5	8.4	5,420	5,420
Diamond Shamrock/ Delaware City, DE	Process Vent	Incinerator Carbon Adsorber	88.0/88.0 85.3/85.3	1,209.0 134.3	0 28.2	439.9 16.4	5,000 190	5,000 190
	Equipment Leak	Equipment & Work Practices	2.9/2.9	14.7	1.0	9.3	3,160	3,160
Diamond Shamrock/ Battleground, TX	Equipment Leak	Equipment & Work Practices	15.0/15.0	53.2	4.9	20.4	1,360	1,360
Diamond Shamrock/ Mobile, AL	Process Vent	Incinerator Carbon Adsorber	31.9/31.9 30.8/30.8	1,209.0 89.5	0 10.2	437.0 21.9	13,700 710	13,700 710
	Equipment Leak	Equipment & Work Practices	2.0/2.0	13.3	0.7	8.8	4,410	4,410
Diamond Shamrock/ Muscle Shoals, AL	Process Vent	Incinerator Carbon Adsorber	50.6/50.6 49.0/49.0	1,209.0 107.4	0 16.2	627.8 21.0	12,400 430	12,400 430
	Equipment Leak	Equipment & Work Practices	3.7/3.7	16.4	1.2	9.4	2,530	2,530
E.I. DuPont/ Corpus Christi, TX	Process Vent	Incinerator	7.8/7.8	1,209.0	0	492.8	63,300	63,300
	Equipment Leak	Equipment & Work Practices	2.6/2.6	14.2	0.8	9.0	3,400	3,400
Vulcan Materials/ Geismar, LA	Process Vent	Incinerator	5.7/5.7	1,209.0	0	472.0	81,900	81,900
	Equipment Leak	Equipment & Work Practices	2.6/2.6	14.2	0.8	9.0	3,400	3,400

TABLE 6-4. ACHIEVABLE CCl_4 EMISSION REDUCTIONS FOR CHLORINE PRODUCTION FACILITIES

	Nationwide CCl_4 Emission Reduction Mg/Yr		
Cost-effectiveness Range, \$/Mg of VOC	Process[a] Vent	Equipment Leak	Total
Credit	-	-	-
0 - 500	229.4	-	229.4
500 - 1,000	30.8	-	30.8
1,000 - 2,000	-	15.0	15.0
2,000 - 5,000	-	13.8	13.8
>5,000	-	1.6	1.6
TOTAL	260.2	30.4	290.6

[a] Emission reductions presented are for carbon adsorption.

ranges. Cost effectiveness for control of storage tanks is estimated to exceed $25,000/Mg of VOC for all tanks and cost/cost-effectiveness estimates for individual tanks are not presented.

6.1.3.1 Control of Process Vent Emissions. Two options were evaluated for control of process vent emissions: incineration and carbon adsorption. The costs for each option are shown in Table 6-3. Only one facility, Diamond Shamrock in Battleground, Texas, presently controls process vent emissions 98 percent or greater. Therefore, the incinerator control was costed for all other facilities. The estimated cost effectiveness of controlling process vent emissions at each of these six facilities by incineration range from $4,300/Mg of CCl_4 to $81,900/Mg of CCl_4. Since CCl_4 is the only VOC, VOC cost effectiveness is identical.

As discussed in Section 6.1.2, three facilities currently control CCl_4 emissions by carbon adsorption. The estimated costs for carbon adsorber control at the remaining four facilities are presented in Table 6-3. The cost effectiveness of this control is significantly less than incineration ranging from $170/Mg of CCl_4 to $710/Mg of CCl_4. The total emission reduction achievable by this control is estimated at 260 Mg/yr. This is 89 percent of current estimated process vent emissions and 73 percent of total emissions from these chlorine production facilities.

6.1.3.2 Controls for Equipment Leak Emissions. The costs of controlling equipment leak emissions with techniques required by the benzene fugitive NESHAP were estimated for each facility. These costs are presented in Table 6-3. The cost effectiveness of applying these control techniques is estimated to range from $1,360/Mg of VOC at the Diamond Shamrock/Battleground facility to $5,420/Mg of VOC at the Diamond Shamrock/Deer Park facility. Equipment count data were not supplied by DuPont and Vulcan. For these two facilities, the costs and emission reduction were estimated to be the average of the four similar Diamond Shamrock facilities.

6.2 DILUENT FOR NITROGEN TRICHLORIDE

Another use of CCl_4 by chlorine producers is as a diluent for nitrogen trichloride (NCl_3). Approximately 380 Mg of CCl_4 were used for this purpose in 1983. Four companies reported that CCl_4 is used as a NCl_3 diluent at one or more facilities. All four companies, Dow Chemical, DuPont, FMC Corporation, and the B.F. Goodrich Company, indicated that CCl_4 is used in a completely enclosed system with no process vents.[5-8] The used CCl_4 is collected for disposal. A list of identified users is presented in Table 6-5 along with estimated emissions.

6.2.1 Process Description

In the production of chlorine, salt (NaCl) is electrolytically reacted with water to form chlorine (Cl_2), sodium hydroxide, and hydrogen. Ammonia (NH_3) is often an impurity in the salt feed and is converted to NCl_3 in the electrolytic cell. From the anodes of the electrolytic cells hot chlorine gas containing considerable amounts of water and small quantities of NCl_3 vapor is evolved. This gas is cooled to condense out the water and then dried with sulfuric acid. This gas is then compressed and cooled to liquify the chlorine. The product or liquefied chlorine contains small quantities of NCl_3.

The chlorine to be liquefied may be passed through a bubble-cap column countercurrent to liquid chlorine. Liquid chlorine is evaporated causing the NCl_3 to build up in recirculating liquid chlorine. The NCl_3 is very unstable even at relatively low concentrations and CCl_4 is added to the chlorine column bottoms to dilute the NCl_3. Chlorine is reclaimed from the bottoms mixture and the CCl_4, NCl_3, and small amounts of chlorine are disposed of as hazardous waste.

6.2.2 Current Controls and Estimated Emissions

The estimated emissions for each facility are presented in Table 6-5. As shown in Table 6-5, estimated emissions are relatively small, totalling only 1 Mg/yr. These estimates are based on the combined emission information

TABLE 6-5. ESTIMATED 1983 EMISSIONS OF CCl_4 FROM USE AS A DILUENT FOR NCl_3 IN CHLORINE LIQUEFACTION (Mg)

Company/Location	Equipment Leak	Storage	Handling	Equipment Opening	Secondary	Total
Dow Chemical/[5] Plaquemine, LA	0.23	0.015	0.015	0.015	-	0.27
Dow Chemical/[6] Freeport, LA	0.045	0.008	0.008	0.008	-	0.07
E.I. duPont/[1] Corpus Cristi, TX	0.14[a]	-	0.013[b]	0.01[a]	-	0.16
FMC Corporation/[7] South Charleston, WV	0.14[a]	-	0.015	-	0.06	0.22
B.F. Goodrich/[8] Calvert City, KY	0.14[a]	-	0.013[b]	0.01[a]	-	0.16
B.F. Goodrich/[8] Convent, LA	0.14[a]	-	0.013[b]	0.01[a]	-	0.16
Total	0.8	0.02	0.08	0.05	0.06	1.0

[a] Estimate based on Dow responses.

[b] Estimate based on Dow and FMC Corporation responses.

received from FMC Corporation and Dow Chemical in Section 114 responses. Only FMC completed the questionnaire on emissions. However, equipment counts for estimating equipment leak emissions were not supplied. Dow estimated the annual equipment leak emissions to be less than 500 pounds and 100 pounds for their Plaquemine and Freeport facilities, respectively.[5,6] The average for these two facilities was used to estimate equipment leak emissions for other facilities.

A material balance of carbon tetrachloride use as a diluent is presented in Figure 6-2. The majority of carbon tetrachloride used for this purpose is reclaimed for disposal. As shown in Figure 6-2, about 0.93 Mg of CCl_4 are disposed of for every Mg used. Most of the remaining CCl_4, 0.068 Mg, ends up in the chlorine product. A small portion, about 1.6 kg per Mg used, may be emitted to the atmosphere.

There are no applicable regulatory requirements for CCl_4 emissions from these facilities.

Cost estimates for control of these emissions were not developed because there are no process vents and fugitive and storage emissions are minimal.

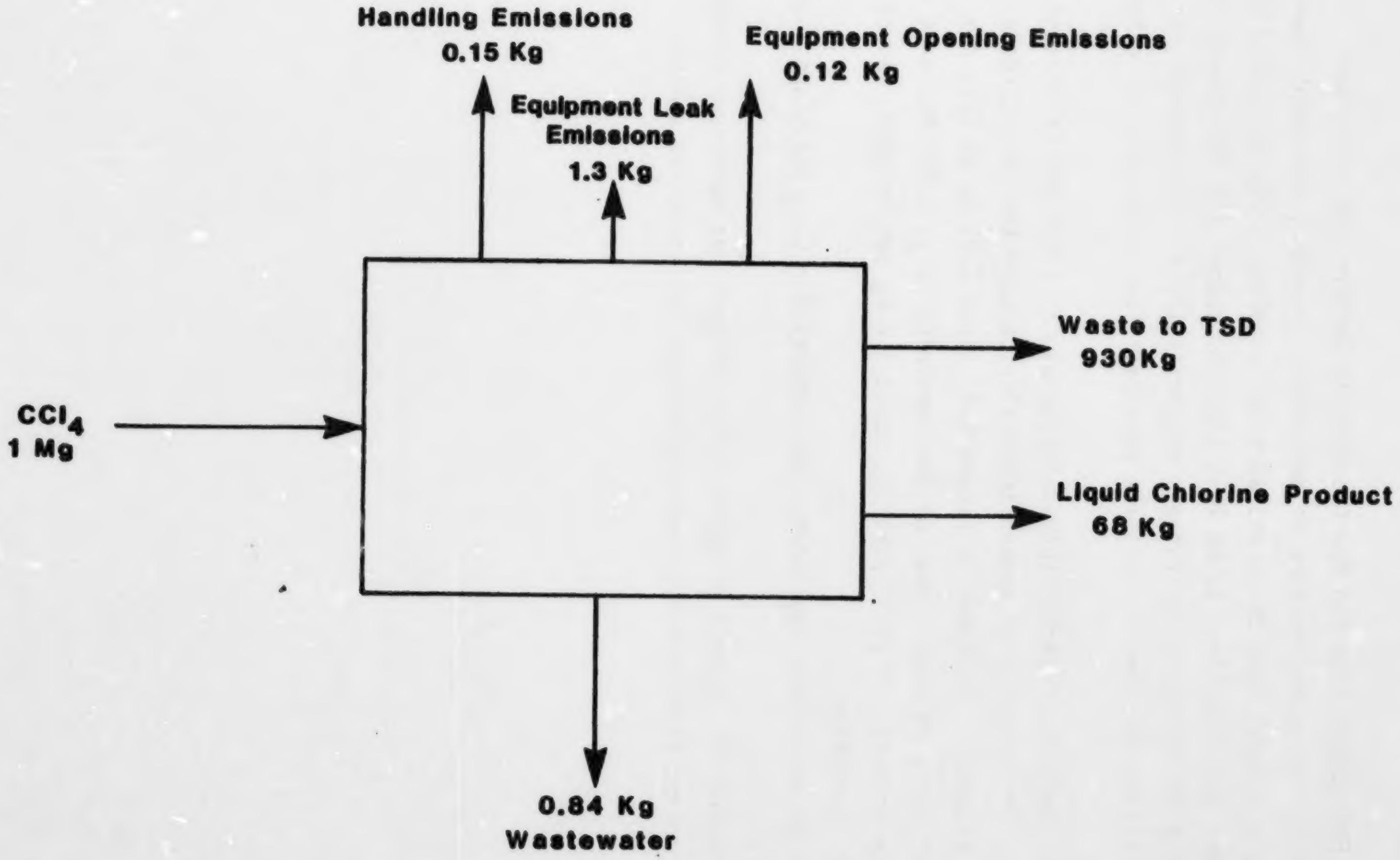
Handling Emissions
0.15 Kg
Equipment Leak
Emissions
1.3 Kg
Equipment Opening Emissions
0.12 Kg
CCl_4
1 Mg
Waste to TSD
930 Kg
Liquid Chlorine Product
68 Kg
0.84 Kg
Wastewater

Figure 6-2. Material balance for use of CCl_4 as a diluent for NCl_3.

6.3 REFERENCES

1. Telecon. J. Harris, E.I. duPont, with R. H. Howle, Radian Corporation. February 25, 1985. Conversation about captive uses of CCl_4.
2. SRI International. 1984 Director of Chemical Producers - United States. SRI International, Menlo Park, California, 1984, pp. 490-491.
3. Letter and attachments from B. H. Christensen, Diamond Shamrock Company, to J. R. Farmer, EPA:ESED. February 14, 1985. Response to Section 114 Letter.
4. Letter and attachments from R. E. Berg, Vulcan Chemicals, to J. R. Farmer, EPA:ESED. January 31, 1985. Response to Section 114 Letter.
5. Letter from S. L. Arnold, Dow Chemical, U.S.A. to J. R. Farmer, EPA:ESED. March 12, 1985. Response to Section 114 Letter.
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7. Letter and attachments from M. T. Chow, FMC Corporation to J. R. Farmer, EPA:ESED. March 11, 1985. Response to Section 114 Letter.
8. Letter from W. C. Holbrook, The B.F. Goodrich Company to J. R. Farmer, EPA:ESED. December 11, 1984. Response to Section 114 Letter.

7.0 HYPALON^R SYNTHETIC RUBBER PRODUCTION

Hypalon^R is the tradename for a synthetic rubber produced by E.I. Dupont de Nemours & Company. Hypalon^R is produced by reacting polyethylene with chlorine and sulfur dioxide, transforming the thermoplastic polyethylene into a vulcanizable elastomer. The reaction is conducted in a solvent (CCl_4) reaction medium.[1] The Dupont plant in Beaumont, Texas is the only facility in the United States producing Hypalon^R. No flow diagram for Hypalon^R is presented because the process is considered confidential by Dupont.

7.1 CURRENT CONTROLS AND EMISSIONS

The primary types of CCl_4 emissions from the Hypalon^R process are process and fugitive emissions. Storage, handling, relief valve discharge, and equipment opening losses were also reported and are summarized in Table 7-1. Annual CCl_4 emissions from this facility are about 220 Mg. The emission types/sources and their controls are discussed below and are summarized in Table 7-2.

The production of Hypalon^R at Dupont's plant in Beaumont, Texas result in about 100 Mg of CCl_4 process vent emissions annually. The largest emitting process vent is controlled by a carbon adsorber. DuPont reported that the efficiency of the carbon absorber was greater than 98 percent. The controlled emissions from this vent are estimated to be about 61.1 Mg. There are nine other dryer basement air exhaust stacks. The emissions from these stacks range from 3.28 to 6.9 Mg/yr. These emissions are not controlled. State VOC gas stream regulations for non-attainment areas exempt streams emitting less than 45.4 kg (100 lb) of VOC in any consecutive 24 hour period. These streams are below the cut-off.

Equipment leak emissions account for about half, 110 Mg, of the annual CCl_4 emissions. DuPont reported that the air at each of about 52 key points

TABLE 7-1. SUMMARY OF 1983 CCl_4 EMISSIONS FROM HYPALON^R PRODUCTION FACILITIES (Mg/Yr)

Plant/Location	Process	Equipment Leak	Relief Devices	Equipment Openings	Storage	Loading Handling	Secondary	Total
E.I. Dupont Beaumont, TX	100.4	110.6	2.1	0.02	2.2	0.4	4.2	220

TABLE 7-2. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT HYPALON^R PRODUCTION FACILITIES

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/yr)	Comments
E.I. Dupont[2] Beaumont, TX	Process Vents				
	- carbon adsorber stack	carbon adsorber	98.77	61.1	
	- Dryer basement air exhaust stack #1	None	N/A	6.9	
	- Dryer basement air Exhaust stack #2	None	N/A	5.7	
	- Stack #3	None	N/A	5.7	
	- Stack #4	None	N/A	5.7	
	- Stack #5	None	N/A	3.3	
	- Stack #6	None	N/A	3.3	
	- Stack #7	None	N/A	3.3	
	- Stack #8	None	N/A	3.3	
	- Stack #9	None	N/A	3.3	
	Equipment Leak	None	N/A	110.6	
	Equipment Openings				
	- 3,000 to 5,000 openings	N_2 purge and isolate	N/A	0.02	Estimated openings and emissions. No record kept.
	Storage				
	- Fixed roof tank	Brine cooled condenser	93.9	0.5	20,000 gallons
	- Fixed roof tank	Brine cooled condenser	93.9	0.5	20,000 gallons
	- Fixed roof tank	Brine cooled condenser	93.9	1.2	46,540 gallons
	- Fixed roof tank	Conservation vent	8.0	0.005	5,200 gallons
	- Pressure tank	Carbon adsorber	100.0	0	15,000 gallons
	- Pressure tank	Carbon adsorber	100.0	0	15,000 gallons

TABLE 7-2. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/yr)	Comments
	- Pressure tank	None	N/A	0	7,500 gallons
	- Pressure tank	None	N/A	0	7,500 gallons
	- Pressure tank	None	N/A	0	12,000 gallons
	- Pressure tank	None	N/A	0	12,500 gallons
	- Fixed roof tank	Condenser and carbon adsorber	98	0	50,000 gallons
	- Pressure tank	None	N/A	0	4,000 gallons
	- Pressure tank	None	N/A	0	10,000 gallons
	- Pressure tank	None	N/A	0	880 gallons
	Loading/Handling				
	- Rail tank cars	None	N/A	0.4	Submerged fill
	Secondary				
	- Process wastewater	None	N/A	2.7	Facultative treatment pond
	- Waste from drum dryer	None	N/A	0.8	Landfill
	- Heels from solvent purification column	Incinerator	N/A	0.2	
	- Off-spec reactor charge	None	N/A	0.03	Landfill
	- Sludge interface from CCl_4 tanks	None	N/A	0.007	Landfill
	- Waste polyethylene and CCl_4 mixture	None	N/A	0.3	Landfill
	- Waste Hypalon^R Polymer	None	N/A	0.2	Landfill
	- Contaminated sample bottles, filters, etc.	None	N/A	0.09	Landfill

TABLE 7-2. (Continued)

Company/Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/yr)	Comments
	Relief Valves				
	- 2 Releases	None	N/A	2.1	

N/A Not Applicable

in the work place at the plant is sampled and analyzed for CCl_4 every ten minutes using a "Wilkes-Miran" infrared analyzer system. This system is reported to be effective in maintaining average CCl_4 levels well below the threshold limit value (TLV) of 5 ppm. However, no information was provided on an actual control program for equipment leaks. Therefore, the equipment leak emission estimates are based on uncontrolled emission factors.

Carbon tetrachloride losses from product storage tanks at the DuPont facility are estimated to be approximately 2.2 Mg/yr. Emissions from five fixed roof tanks ranging in size from 20,000 to 52,000 gallons accounted for all the storage emissions. There are also nine pressure tanks ranging in size from 880 gallons to 15,000 gallons at this facility. These tanks are assumed to have minimal emissions. Unless VOC are stored in pressurized tanks, the following regulations apply in Texas.

1) VOC storage tanks between 1,000 and 25,000 gallons must have a submerged fill pipe.
2) VOC storage tanks between 25,000 gallons and 42,000 gallons must have an internal or external floating roof (any type) or a vapor recovery system.
3) VOC storage tanks over 42,000 gallons must have either an internal floating roof, external floating roof with vapor mounted primary seal and secondary seal, or a vapor recovery system.

One 20,000 gallon fixed roof storage tank at DuPont is controlled by a brine cooled condenser and a 50,000 gallon tank is controlled by a condenser and a carbon adsorber. Both tanks meet State emission regulations. A 5,200 gallon fixed roof tank has only a conservation vent, but also has a submerged fill pipe and meets the State regulations.

Losses due to handling of CCl_4 are approximately 0.4 Mg/yr. The CCl_4 raw material is received at the plant in steel railroad tank car lots of about 200,000 lbs. per tank car. One tank car at a time is connected up to an unloading spot. The CCl_4 is pumped from the tank car as needed through a bottom unloading line to the wet CCl_4 storage tanks.

Dupont does not keep records of equipment openings. An estimate was made by Dupont of 3,000 to 5,000 openings in 1983 of equipment containing

10 percent or greater CCl_4. It is standard procedure at the plant to clear all equipment to be opened prior to opening. The equipment is always isolated prior to opening. The clearing is done by pumping or draining all process material in the equipment back to the process and then purging with N_2. This opening procedure has allowed only trace quantities of CCl_4 to be emitted to the atmosphere. Emissions from equipment openings in 1983 were estimated by DuPont to be 0.02 Mg. The state of Texas has no specific regulations regarding equipment opening emissions.

Secondary emissions range from 0.03 Mg/yr for off-spec reactor charge which is landfilled, to 2.7 Mg/yr for process wastewaters treated in a facultative pond. Table 7-2 summarizes the rest of the secondary emission sources and final treatment methods. Secondary emissions are not regulated by the state of Texas.

There were two relief valve discharges in 1983 at the Hypalon^R plant. A total of 2.1 Mg. of CCl_4 were released. Both releases occurred from the Hypalon^R reactor during pressure surges. There are no regulations governing pressure relief device discharges in the State of Texas.

7.2 COST OF ADDITIONAL CONTROLS

Costs of additional controls to reduce present CCl_4 emissions at Dupont's Hypalon^R facility were estimated for process, fugitive and storage sources. A summary of these costs and their cost effectiveness is provided in Table 7-3 and discussed below.

7.2.1 Control of Process Vent Emissions

Additional controls were considered only for those process vent emission sources with no present controls or existing control efficiencies less than 98 percent. The vents on all nine dryer basement air exhaust stacks are presently uncontrolled. Incineration control cost was estimated for reducing the exhaust stack emissions. Controlling emissions by 98 percent would reduce the annual emissions of CCl_4 by about 39.5 Mg. Capital cost of incinerators (5) for control of exhaust stack emissions is $31,900,000. The cost effectiveness of incineration for reducing CCl_4 emissions is $745,000/Mg of VOC.

TABLE 7-3. COSTS FOR ADDITIONAL CONTROLS AT DUPONT'S HYPALON^R FACILITY

Company/ Location	Emission Type/Source	Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M $)	Recovery Credit (M $)	Annual Cost (M $)	CostEffectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
E.I. Dupont Beaumont, TX	Process - Dryer Stacks	Incinerator	40.0/44.0	31,900	-	32,800	820,000	745,000
	Equipment Leak	Equipment & Work Practices	56.8/112	38.8	37.0	16.2	286	145
	Storage Fixed Roof Tank	Refrigerated Condenser	0.0/0.3	110.8	0.0	29.1	665,000	99,800

7.2.2 Control of Equipment Leak Emissions

The equipment leak emissions from Dupont's Hypalon^R facility were estimated using equipment count data supplied in the Section 114 response[2]. Controls required by the benzene fugitive NESHAP were evaluated for controlling equipment leak emissions. The estimated costs and cost effectiveness of controlling equipment leak emissions is summarized in Table 7-3. It is estimated that the equipment leak emissions will be reduced by 51.6 percent at a capital cost of \$38,800. The cost effectiveness of controlling equipment leak emissions is estimated to be \$145/Mg of VOC and \$286/Mg of CCl_4.

7.2.3 Control of Storage Emissions

Additional control with a condenser was costed for 1 of the 5 fixed roof storage tanks at the Dupont facility. Two 20,000 gallon and one 46,540 gallon fixed roof tanks are already controlled by a brine cooled condenser with 93.9 percent efficiency. A 50,000 gallon storage tank also has a condenser and a carbon adsorber for a total reported control efficiency of greater than 98 percent. Additional controls were evaluated for the one 5,200 gallon fixed roof tank. It is estimated that a condenser will provide 83.7 percent control. The cost effectiveness of this control is estimated to be \$99,800/Mg of VOC. Costs for a floating roof was not estimated because a floating roof is not expected to reduce emissions due to the small size of the tank.

7.3 REFERENCES

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2. Letter and Attachments from McClure, R. L., E.I. Dupont Beaumont Works to Farmer, J. R., EPA:ESED. Response to Section 114 Letter. March 15, 1985.

3. U.S. Environmental Protection Agency. Benzene Fugitive Emissions -- Background Information for Promulgated Standard. Research Triangle Park, North Carolina. Publication No. EPA-450/3-80-0326. June 1982.

8.0 PESTICIDE PRODUCTION

Approximately 4,105 Mg of CCl_4 was used in the pesticide industry in 1983. This usage accounts for 1.5 percent of the total CCl_4 consumed that year. Emissions of CCl_4 were reported to be associated with the production of the following pesticides: chlorothalonil, dacthal, and tordon acid. The production of these three pesticides accounts for 1,504 Mg of the total CCl_4 used in the industry. Approximately 2,601 Mg is used in other pesticide production operations at 4 facilities. Carbon tetrachloride is used mainly as a solvent or reaction medium in the pesticide production processes.

Emissions of CCl_4 from the three identified pesticide production processes is approximately 420 Mg/yr. Based on the ratio of emissions to use (0.28 Mg/Mg), the CCl_4 emissions from other pesticide production processes is estimated to be 730 Mg/yr. Therefore, total estimated CCl_4 emissions for the pesticide industry are 1,200 Mg/yr. The identified pesticide production processes are discussed individually in the following sections.

8.1 CHLOROTHALONIL

Chlorothalonil is manufactured in the United States under the tradename Daconil 2787^R and Bravo^R by SDS Biotech Corporation at their Greens Bayou, TX facility. Cited uses include agricultural and horticultural fungicide, bactericide, and nematocide.[1] Chlorothalonil is made by dissolving tetrachloroisophthalic acid chloride in an organic solvent (CCl_4) and adding ammonia.[1] A flow diagram showing the chlorothalonil process cannot be presented because the company considers the information to be confidential.

8.1.1 Current Controls and Emissions

The primary types of CCl_4 emissions from SDS Biotech's Daconil processes are process and equipment leak. Other minor sources of CCl_4

emissions include relief valve discharges, storage, equipment openings, and secondary emissions. These emissions are summarized in Table 8-1 and discussed below. Total CCl_4 emissions from this facility are estimated to be 377 Mg/yr.

There are two Daconil processes at SDS Biotech's facility in Greens Bayou, TX. Process vent emissions are estimated to be 123.6 Mg for Daconil I and 122.3 Mg for Daconil 2. The two Daconil process vent emissions sources are located on the chlorine absorber. Both vents are controlled by freon chillers with greater than 50 percent control efficiency. The plant is located in Harris county and is regulated under the State of Texas nonattainment regulations for VOC's. Emissions from vent streams in Harris County are regulated according to certain VOC classes, which include CCl_4. The vent streams must be burned properly at a temperature equal to or greater than 1300°F (704°C) in a direct flame incinerator before it is allowed to enter the atmosphere. There are exemptions to this regulation. Alternate means of control may be approved by the executive director.

Equipment leak emissions for the Daconil 1 and 2 processes are estimated to be 48.9 Mg/yr and 60.4 Mg/yr, respectively. State regulations requiring a formal equipment leak emissions monitoring program have recently been promulgated. The requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and valves in liquid service, monthly leak detection for compressor seals and valves in gas service, and weekly visual inspection of pump seals. Repair or reasonable measures to minimize identified leaks is required within 15 days. Also, open-ended lines are required to be capped.

Losses from CCl_4 storage were estimated to be 0.015 Mg/yr for Daconil 1 and 0.043 Mg for Daconil 2 based on 1983 storage data. Storage tanks in Harris County with a capacity greater than 42,000 gallons (158,487 liters) are required to have an internal floating roof, external floating roof, or vapor recovery system which returns vapor to a disposal system. An external roof must have primary and secondary seals between the tank wall and roof edge.

TABLE 8-1. SUMMARY OF 1983 CCl_4 EMISSIONS FROM PESTICIDE PRODUCTION FACILITIES (Mg)

Plant/Location	Process	Equipment Leak	Relief Devices	Equipment Openings	Storage	Loading/ Handling	Secondary	Total
SDS Biotech/ Greens Bayou, TX[2]								
Daconil 1	123.6	48.9	0.06	0.57	0.015	0	0.27	173.4
Daconil 2	122.3	60.4	0.52	0.73	0.043	0	0.47	184.5
Dachtal^R	17.4	10.0	0	0.16	0.80	0	0	28.4
Dow Chemical/ Freeport, TX[3]								
Tordon Acid	0.015	33.9	0	0.027	0.0003	0.11	0	34.0
TOTAL	263.3	153.2	0.58	1.5	0.86	0.11	0.74	420.3

The Daconil 1 unit had 29 equipment openings in 1983 with estimated CCl_4 emissions of 0.57 Mg. The Daconil 2 unit also had 29 equipment openings resulting in 0.73 Mg of CCl_4 emissions. The State of Texas has no specific regulations regarding equipment opening emissions.

SDS Biotech reported that secondary emissions in 1983 were 0.27 Mg from the Daconil 1 process and 0.47 Mg from Daconil 2 process.

There were three relief valve discharges in 1983 from the Daconil 1 process. Approximately 0.06 Mg of CCl_4 were released. The Daconil 2 process had seven releases emitting approximately 0.52 Mg of CCl_4. There are no regulations governing these pressure relief device discharge emissions in Texas.

8.2 DACTHAL^R PRODUCTION

Dacthal^R is manufactured under the common name of DCPA or DAC by SDS Biotech Corporation in Greens Bayou, TX.[1] It is used as a selective preemergence herbicide.[1] The production process and flow diagram are considered confidential business information by the manufacturer.

8.2.1 Current Controls and Emissions

The primary sources of CCl_4 emissions from SDS Biotech's Dacthal^R process are process and equipment leak. Emissions from these sources are summarized in Table 8-1 and discussed below.

There two process emission sources from the Dachtal manufacturing process. The photochlorination reactor vent with estimated CCl_4 emissions of 4.2 Mg/yr and the thermal chlorination reactor vent with estimtaed CCl_4 emissions of 13.2 Mg/yr. Both vents are controlled by condensers with reported efficiencies of 85 percent and 79 percent, respectively.

The SDS Biotech facility is located in Harris County, Texas and is covered by State emissions standards. Both vent streams are exempt from Harris County process emission regulations since they are under 45.4 kg/24 hour period (11.5 kg/24 hr and 36.2 Kg/24 hr).

Equipment leak emissions from the Dachtal process were estimated to be 10 Mg/yr. State regulations have recently been promulgated requiring a formal equipment leak control program to be completed by the end of 1987. This program was discussed in the previous section.

Annual emissions from CCl_4 storage are estimated to be 0.80 Mg for the Dachtal process based on 1983 storage tank data.

The Dachtal CCl_4 storage emissions are minimal due to present controls. The storage tanks emissions are within the Harris County regulation limits for VOC.

8.3 TORDON ACID

Tordon acid is manufactured in the U.S. by Dow Chemical. Another common name for tordon acid is pichloram.[1] It is a systemic herbicide effective against a wide variety of deep-rooted herbaceous weeds and woody plants. It is sold for noncrop use in brush control along utility rights-of-way, for weed and brush control in pastures and rangeland, and broadleaf weed control in small grains production.[1]

Dow considers the manufacturing process for tordon acid to be confidential business information and, therefore, no description or flow diagram is provided.

8.3.1 Current Controls and Emissions

The primary source of CCl_4 emissions from the manufacture of tordon acid is equipment leaks. Equipment leak emissions were estiamted at 33.9 Mg/yr. Emissions from this source and other minor sources are summarized in Table 8-1.

Dow manufactures the tordon acid at their plant in Freeport, Texas and is subject to Texas air regulations for Harris County. Dow currently meets Harris County regulations with the control equipment they have in place.

8.4 COST OF ADDITIONAL CONTROLS

Cost estimates were developed for control of process vent, fugitive, and storage emissions at the pesticide manufacturing facilities discussed earlier. The cost effectiveness of controlling the emissions from these sources is summarized in Table 8-2 and discussed in the following sections.

Table 8-3 summarizes the estimated CCl_4 emission reductions as a function of cost effectiveness. The emission reductions are separated by type and totalled for the identified pesticide CCl_4 users. If all additional controls were put in place, a 77 percent (324 Mg/yr) reduction in CCl_4 emissions would be possible from the two pesticide facilities.

8.4.1 Control of Process Vent Emissions

Additional control by incineration was considered only for those process vent emission sources currently not controlled greater than 98 percent. The cost effectiveness for controlling process emissions ranged from $3,700/Mg of VOC to $24,700/Mg of VOC. Carbon tetrachloride process vent emissions could be reduced by 98 percent (257.9 Mg) if the pesticide plants implemented incinerator controls.

8.4.2 Control of Equipment Leak Emissions

Estimated costs for controlling equipment leak emissions are based on control techniques required by the benzene fugitive NESHAP. The cost effectiveness of controlling equipment leak emissions from pesticide plants ranged from $200/Mg of VOC to $1,600/Mg of VOC. By controlling CCl_4 equipment leak emissions at these two facilities, total CCl_4 equipment leak emissions could be reduced by 41 percent or 63.3 Mg/yr.

8.4.3 Control of Storage Emissions

Cost estimates were developed for control of fixed-roof storage tank emissions which currently do not have greater than 85 percent control efficiency. Dow uses incineration to control storage tank emissions greater than 98 percent and SDS Biotech's Daconil process storage tanks are

TABLE 8-2. COSTS FOR ADDITIONAL CONTROLS AT PESTICIDE PRODUCTION FACILITIES

Company/Location	Emission Type/Source	Control	Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Dow Chemical Freeport, TX								
Tordon Acid	Equipment Leak	Equipment & Work Practices	18.1/35.9	7.8	11.8	7.1	400	200
SDS Biotech Greens Bayou, TX								
Daconil 1	Process	Incinerator	121.1/121.1	1,209	0	449.6	3,700	3,700
	Equipment Leak	Equipment & Work Practices	18.1/31.6	62.3	10.4	21.2	1,200	700
Daconil 2	Process	Incinerator	119.8/119.8	1,209	0	469.2	3,920	3,920
	Equipment Leak	Equipment & Work Practices	22.3/42.9	74.6	14.1	27.2	1,200	600
Dachtal^R	Process	Incinerator	17.0/17.0	1,209	0	420.2	24,700	24,700
	Equipment Leak	Equipment & Work Practices	4.8/5.9	17.1	1.9	9.6	2,000	1,600
	Storage	Int. Floating Roof-PO	0.1/0.1	15.3	0	4.0	60,100	59,500
		Int. Floating Roof-SS	0.1/0.1	17.6	0	4.6	47,200	46,700
		Refrigerated Condenser	0.3/0.3	110.8	0.1	29.0	90,200	89,300

PO - Primary seal only.
SS - Primary and secondary seals.

TABLE 8-3. ESTIMATED CCl_4 EMISSION REDUCTIONS AS A FUNCTION OF COST EFFECTIVENESS

Cost-Effectiveness Range, \$/Mg of VOC	Nationwide CCl_4 Emission Reduction (Mg/yr)			
	Process	Equipment Leak	Storage	Total
Credit	-	-	-	-
0 - 500	-	18.1	-	18.1
500 - 1,000	-	40.4	-	40.4
1,000 - 2,000	-	4.8	-	4.8
2,000 - 5,000	240.9	-	-	240.9
>5,000	17.0	-	0.3	17.3
TOTAL	257.9	63.3	0.3	321.5

[a] Emission reductions presented are for carbon adsorption.

controlled using a confidential method. Only the Daconil storage tanks need additional controls. The three control options evaluated were: contact internal floating roof with primary seal (FR-PO), contact internal floating roof with primary and secondary seal (FR-SS), and a refrigerated condenser. The cost effectiveness ranged from $46,700/Mg of VOC using FR-SS to $89,300/Mg of VOC with the condenser.

8.5 REFERENCES

1. Farm Chemicals Magazine. Farm Chemicals Handbook. Meister Publishing Company, New York, 1984.

2. Letter and attachments from J. E. Stansbury, SDS Biotech Corporation to J. R. Farmer, EPA:ESED. April 15, 1985. Response to Section 114 Letter.

3. Letter and attachments from S. L. Arnold, Dow Chemical, U.S.A. to J. R. Farmer, EPA:ESED. March 1985. Response to Section 114 Letter.

9.0 CHLORINATED PARAFFINS PRODUCTION

Chlorinated paraffins are mainly straight-chain, saturated hydrocarbons of the C_{10} - C_{30} range. The manufacturing process consists of passing gaseous chlorine into a paraffin hydrocarbon.[1] In some processes, (dry chlorinated paraffins) chlorination is carried out by using solvents, such as CCl_4, under reflux. Paraffins of this type, containing 70 percent or greater chlorine, contain residual amounts of CCl_4 which may be released into the atmosphere.

Currently, there is only one producer of dry chlorinated paraffins (resinous chlorowax) using CCl_4 solvent in the United States.[2] This Diamond Shamrock facility is located in Deer Park, Texas. The process by which chlorinated paraffins are produced is considered confidential by Diamond Shamrock.

9.1 CURRENT CONTROLS AND EMISSIONS

The total CCl_4 emissions from the Diamond Shamrock chlorinated paraffins plant is estimated to be about 9.4 Mg/yr. Table 9-1 summarizes the emissions of CCl_4 from this plant. The emission types/sources and their controls are discussed below and listed in Table 9-2.

Emissions from process vents at the Diamond Shamrock plant in Deer Park, Texas are estimated to be 0.8 Mg of CCl_4 at full capacity. The vents are located on a stripper chiller and three surge tanks. The largest emission source was 0.53 Mg from one of the dry CCl_4 surge tank vents. The control device on this emission source is a vent chiller with 84.5 percent removal efficiency. The next largest emission source resulting in 0.26 Mg of CCl_4 emissions, is another surge tank vent. This vent is also controlled by a vent chiller with a 89.2 percent removal efficiency. The remaining two vents emit less than 0.001 Mg/yr of CCl_4. One of these vents is controlled by a condenser, decanter and vent chiller (greater than 98 percent control efficiency) while the other vent has a vent chiller which is intended to control emissions in the event that the water blanket is lost.

TABLE 9-1. SUMMARY OF ESTIMATED 1983 CCl_4 EMISSIONS FROM THE DIAMOND DIAMOND SHAMROCK CHLORINATED PARAFFINS PRODUCTION FACILITY (Mg)

Plant/Location	Process	Equipment Leak	Secondary	Total
Diamond Shamrock[3] Deer Park, TX	0.8	8.3	0.31	9.4

TABLE 9-2. CURRENT CONTROLS AND ESTIMATED 1983 EMISSIONS AT THE DIAMOND SHAMROCK CHLORINATED PARAFFINS FACILITY

Company/ Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
Diamond Shamrock[3]	Process				
Deer Park, TX	- Stripper Chiller Vent	Condenser, decanter and vent chiller	98.0[a]	0.001	
	- Surge tank vent	Vent chiller	NR	0.001	
	- Surge tank vent	Vent chiller	84.5	0.53	
	- Surge tank vent	Vent chiller	89.2	0.26	
	Equipment Leak	None	N/A	8.3	
	Equipment Openings	-	-	Minimal	No records kept; closed system
	Storage	-	-	0	CCl_4 received directly into system
	Loading/Handling	Vent chiller	NR	Minimal	CCl_4 shipments by tank trucks; vented to vent chiller
	Secondary				

TABLE 9-2. (Continued)

Company/ Location	Type of Emission/Source	Present Controls	Reported Control Efficiency (%)	Present CCl_4 Emissions (Mg/Yr)	Comments
	- Wastewater	None	N/A	0.31	Combined with wastewater from PCE process, steam stripped, and pumped to biological treatment plant.

N/A Not Applicable
NR Not Reported

[a] Company reported greater than 98 percent control, but only 98 percent is accepted without supporting test data.

Texas regulations for vent streams in Harris County specify that certain VOC classes, which include CCl_4, must be burned properly at a temperature equal to or greater than 1300°F (704°C) in a smokeless flare or direct flame incinerator before it is allowed to enter the atmosphere. However, all of the vent streams at Diamond Shamrock are exempt from this regulation. The vent with the largest quantity of CCl_4 emissions at Diamond Shamrock releases an average of only 0.39 kg/hr (9.35 kg. in any 24 hour period) which is well below the 45.5 kg/24 hr exemption.

Equipment leak emissions account for 88 percent of the total CCl_4 emissions from chlorinated paraffins production, totalling 8.3 Mg/yr. Diamond Shamrock indicated that there is currently no formal monitoring and control program for equipment leaks. Operating personnel are instructed to report any leaking components that they observe on their normal rounds. The Texas Air Control Board has recently promulgated regulations for Harris County that will require a formal equipment leak monitoring program. Requirements include annual leak detection (greater than 10,000 ppm VOC) for pump seals and valves in liquid service, monthly leak detection for compressor seals and valves in gas service, and weekly visual inspection of pump seals. Repair or reasonable measures to minimize identified leaks is required within 15 days. Also, open-ended lines are required to be capped.

There were no losses from storage because all CCl_4 is received directly into the production system.

All CCl_4 shipments are received in tank trucks. The tank trucks are hooked up directly to either the dry CCl_4 tank or the wet CCl_4 tank. During unloading, the displaced gas is vented through the respective vent chiller. The trucks are unloaded by pressure and are kept closed. Unloading emissions are considered minimal by the plant because of the effectiveness of the chillers.

The State of Texas requires a vapor recovery system for emissions from loading and unloading of a VOC with a true vapor pressure equal to or greater than 1.5 psia (10.3 kPa) under actual storage conditions. In addition, the facility must have 20,000 gallons (75,708 liters) or more throughput per day (averaged over any consecutive 30-day period) to be affected by this regulation. Diamond Shamrock's total VOC throughput is not known and therefore, it is not known if the regulation applies to their facility.

Diamond Shamrock does not keep records of equipment openings. However, the plant reported that the production process is a closed system and equipment openings are infrequent. Standard procedure for maintenance opening of equipment at Diamond Shamrock is to drain all liquid and purge with steam or nitrogen to remove the lost traces of chemicals prior to opening. The State of Texas has no specific regulations regarding equipment opening emissions.

The only source of secondary CCl_4 emissions at the Diamond Shamrock facility is from wastewater treatment. About 0.31 Mg/yr (0.86 kg/day) of CCl_4 emissions occur when the chlorinated water is combined with wastewater from the perchloroethylene process, steam stripped, and pumped to a biological water treatment plant for final treatment.

9.2 COSTS OF ADDITIONAL CONTROLS

Costs of additional controls to reduce present CCl_4 emissions at Diamond Shamrock's dry chlorinated paraffins plant were estimated for process and fugitive emission sources. A summary of the costs and cost effectiveness is provided in Table 9-3 and discussed below.

9.2.1 Control of Process Vent Emissions

Additional emission controls were considered for those process sources with no present controls or existing control efficiencies less than 98 percent. The stripper chiller vent emissions at Diamond Shamrock's dry chlorinated paraffins plant is reportedly controlled greater than 98 percent by a condenser, decanter and vent chiller. The vents on the three surge tanks have vent chillers, with different control efficiencies. A control efficiency was not reported for the first CCl_4 surge tank vent chiller. The second CCl_4 surge tank vent chiller has a 84.5 percent control efficiency and the third surge tank vent chiller a 89.2 percent control efficiency.

TABLE 9-3. COSTS FOR ADDITIONAL CONTROLS AT THE DIAMOND SHAMROCK CHLORINATED PARAFFINS FACILITY

Company/ Location	Emission Type/Source	Control	CCl_4/VOC Emission Reduction (Mg/Yr)	Capital Cost (M$)	Recovery Cost (M$)	Net Annual Cost (M$)	Cost Effectiveness CCl_4 ($/Mg)	Cost Effectiveness VOC ($/Mg)
Diamond Shamrock/ Deer Park, Texas	Process							
	3 surge tank vents	Incineration	0.8/0.8	1,228	-	415.6	534,000	534,000
	Equipment Leak	Equipment & Work Practices	3.8/6.8	11.7	2.2	5.0	1,310	730

The cost for an incinerator was estimated for all three surge tank vents. It was assumed that the emission streams from all three tanks will be combined and directed to one incinerator. The cost effectiveness of this control device is estimated at \$534,000/Mg of CCl_4 emission reduction. Carbon tetrachloride process vent emissions would be reduced by 98 percent or 0.8 Mg/yr.

Cost of controls for fugitive emissions were estimated based on control techniques required under the benzene fugitives NESHAP. The cost effectiveness of fugitive emissions control at the chlorinated paraffins plant is estimated to be \$1,310/Mg of CCl_4 and \$730 Mg of VOC. Carbon tetrachloride emissions would be reduced by 3.8 Mg/yr (45 percent) as a result of equipment leak controls.

9.3 REFERENCES

1. Kirk - Othmer. Encyclopedia of Chemical Technology: Volume 5. John Wiley and Sons Inc., New York, 1977.

2. Telecon. Howle, R.; Radian Corporation, with Christensen, B. H.; Diamond Shamrock. General Information on Usage of Carbon Tetrachloride in Production of Chlorinated Paraffins. January 2, 1985.

3. Letter and attachments for Christensen, B. H., Diamond Shamrock to Farmer, J.R., EPA:ESED, Response to Section 114 Letter. January 21, 1985.

10.0 PHARMACEUTICAL MANUFACTURING

There are currently about 800 pharmaceutical plants in the United States and its territories. Carbon tetrachloride is sometimes used as a solvent in the manufacturing of pharmaceutical products. The trend, according to several of the major pharmaceutical firms contacted, is to reduce CCl_4 usage. This is supported by information supplied by CCl_4 producers. Carbon tetrachloride consumption by pharmaceutical manufacturers in 1983 is estimated to be 231 Mg. This consumption can be compared to an estimated 1,850 Mg of consumption by 26 ethical drug manufacturers in 1978.[1]

10.1 ESTIMATED EMISSIONS

A survey of 26 ethical drug manufacturers published in 1978 cites a total annual CCl_4 purchase of 1,850 Mg (2,030 tons) by these manufacturers.[1] The survey was estimated to cover about 85 percent of all volatile organic compounds used by the reporting manufacturers, who accounted for 53 percent of domestic sales of ethical pharmaceuticals in 1975. Estimated final disposition of the above total CCl_4 usage was reported as 210 Mg (230 tons) air emissions (11 percent), 120 Mg (130 tons) sewer disposal (7 percent), and 1,510 Mg (1,660 tons) incineration (82 percent). The survey did not provide data on individual plants, processes, or related CCl_4 use. Assuming the same disposition for 1983 consumption, estimated air emissions are 26 Mg.

Available controls for CCl_4 emissions include condensers, scrubbers, and carbon adsorbers. Storage and transfer emissions can be controlled by vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks. Although control efficiencies may vary with the specific process, overall control of 90 percent of CCl_4 emissions or better is generally possible.

The best CCl_4 emission control method and the one being adopted by the pharmaceutical industry is total elimination of CCl_4 as a solvent. From telephone discussions with various pharmaceutical manufacturers, it was established that the industry as a whole is attempting to eliminate CCl_4 usage.[2-4]

10.2 REFERENCES

1. U.S. Environmental Protection Agency. Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products. Research Triangle Park, N.C. Publication No. EPA/450/2-78-029. December 1978. pp. 2-2 through 2-5 and Appendix A.

2. Telecon. White, T., Pharmaceutical Manufacturers Association, with Kowalski, J. A., Radian Corporation, January 2, 1985. General Information on Carbon Tetrachloride Usage in Pharmaceutical Production.

3. Telecon. Visser, M., Upjohn Co., with Howle, R., Radian Corporation. April 19, 1985. Conversation on use of CCl_4.

4. Telecon. Robertson, B., Abbot Labs, with Howle, R., Radian Corporation. April 17, 1985. Conversation on use of CCl_4.

11.0 MISCELLANEOUS PRODUCTION USES OF CARBON TETRACHLORIDE

Approximately 145 Mg of CCl_4 were emitted from miscellaneous chemical production processes in 1983. These miscellaneous chemical products are produced by Dow Chemical Company. They include symmetrical tetrachloropyridine and two confidential processes which are labeled Confidential process 1 and 2 for identification purposes.

11.1 SYMMETRICAL TETRACHLOROPYRIDINE[1]

The symmetrical tetrachloropyridine process is currently used at Dow facilities in Freeport, Texas and Pittsburg, California. The symmetrical tetrachloropyridine process is considered confidential by Dow and will not be discussed in any detail.

11.1.1 Current Controls and Emissions

The primary types of emissions from this process are process vent, equipment leak, and storage. In addition, relatively small emissions occur from equipment openings and from handling at the two facilities. A summary of emissions by facility and type is presented in Table 11-1.

Process vent emissions from the Freeport, Texas facility were 0.27 Mg in 1983. The facility is exempt from the Brazoria County, Texas regulations for process emissions because these emissions are below the 45.5 kg/24 hour exemption.

Equipment leak emissions are the largest type of CCl_4 emissions generated by symmetrical tetrachloropyridine production. Approximately 57 Mg were emitted from the Freeport, Texas facility and 9.4 Mg from the Pittsburg, California facility. There are no State regulations in Brazoria County for equipment leak emissions.

The symmetrical tetrachlorpyridine facility located in Pittsburg, California is regulated by the Bay Area District. The regulations require

TABLE 11-1. SUMMARY OF 1983 CCl_4 EMISSIONS FROM MISCELLANEOUS PRODUCTION FACILITIES (Mg)

Plant/Location	Process	Equipment Leak	Relief Devices	Equipment Openings	Storage	Loading/ Handling	Secondary	Total
Dow Chemical/Freeport, TX[1] (Symmetrical Tetrachloropyridine)	0.27	57.0	0	0.025	0.75	0.004	0	58.1
Dow Chemical/Pittsburg, CA[1] (Symmetrical Tetracloropyridine)	0.68	9.4	0	0.008	0	0	0	10.0
Dow Chemical/Midland, MI[1] (Confidential Process 1)	9.4	39.7	0.12	0.01	0	0.04	9.1	58.3
Dow Chemical/Allyn's Pt., CT[2] (Confidential Process 2)	0.54	2.8	0.045	0.045	0.032	0.13	0.082	3.7
Dow Chemical/Dalton, GA[2] (Confidential Process 2)	0.54	2.8	0	0.045	0.032	0.13	0.082	3.6
Dow Chemical/Freeport, TX[2] (Confidential Process 2)	0.54	2.8	0	0.045	0.032	0.13	0.082	3.6
Dow Chemical/Midland, MI[2] (Confidential Process 2)	0.54	2.8	0	0.045	0.032	0.13	0.082	3.6
Dow Chemical/Pittsburg, CA[2] (Confidential Process 2)	0.54	2.8	0	0.045	0.032	0.13	0.082	3.6
TOTAL	13.0	119.9	0.16	0.27	0.91	0.70	9.51	144.5

annual inspections of all valves and flanges and repair within six months. Dow has indicated that a formal leak detection and repair program is currently in use. However, the emissions reduction due to an annual leak detection and repair program is considered minimal by EPA.

Losses from product storage were estimated to be 0.75 Mg/yr for the Freeport, Texas facility while the Pittsburg, California facility reported no storage emissions.

11.2 DOW CONFIDENTIAL PROCESS 1[1]

Dow's Confidential process 1 is used at their facility in Midland, Michigan. The product and the process are both considered confidential by Dow and will not be discussed in any detail.

11.2.1 Current Controls and Emissions

The primary types of emissions from this process are process vent, equipment leak, and secondary emissions. In addition, relatively small emissions occur from handling, equipment openings, and relief device discharges. A summary of the emissions is presented in Table 11-1.

Process emissions were 9.4 Mg in 1983. These emissions accounted for 16 percent of the total CCl_4 emissions from the facility. There are no State regulations in Michigan requiring control of VOC emissions from process vents.

Sixty-eight percent (39.7 Mg) of the total emissions from this process are fugitive emissions which are not controlled by Federal or State regulations. Secondary emissions are another major emission source accounting for 16 percent (9.1 Mg) of the total CCl_4 emissions in 1983. Other emissions are 0.12 Mg/yr for relief devices, 0.01 Mg/yr for equipment openings, and 0.04 Mg/yr during handling.

11.3 DOW CONFIDENTIAL PROCESS 2[2]

Dow's Confidential process 2 is used at five different facilities. These facilities are located in Pittsburg, California; Midland, Michigan; Freeport, Texas; Dalton, Georgia; and Allyn's Pt., Connecticut. A summary of the emissions by facility and type is presented in Table 11-1. It should be noted that Dow's response gave emissions for a model plant applicable to all five facilities rather than the actual facilities. The process and product are considered confidential by Dow and will not be discussed in any detail.

11.3.1 Current Controls and Emissions

The primary types of emissions from these facilities are process vent and equipment leak emissions. In addition, small emissions occur from relief device discharges, equipment openings, storage, handling and secondary sources. A summary of the emissions by type is presented in Table 11-1.

Process emissions were 0.54 Mg in 1983 for the model plant. These emissions accounted for 15 percent of the total CCl_4 emissions from the facilities. Seventy-eight percent (2.8 Mg) of the total estimated CCl_4 emissions from this process are equipment leak emissions. Storage emissions account for less than 1.0 percent (0.032 Mg/yr) of the total CCl_4 emissions while handling emissions were estimated to make up about 3 percent (0.13 Mg/yr) of the total model plant emissions.

11.4 COST OF ADDITIONAL CONTROLS

Costs of additional controls to reduce present CCl_4 emissions at all Dow facilities covered in this chapter were estimated for process vent, equipment leak, and storage sources. A summary of the costs and their cost effectiveness is provided in Table 11-2 and discussed below.

11.4.1 Control of Process Vent Emissions

The cost of controlling process vent emissions for miscellaneous processes at Dow's facilities were developed for incineration control.

TABLE 11-2. COSTS FOR ADDITIONAL CONTROLS AT MISCELLANEOUS PRODUCTION FACILITIES

Company/Location	Emission Type/Source	Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness CCl_4 ($/Mg)	Cost Effectiveness VOC ($/Mg)
Dow Chemical/ Freeport, TX (Symmetrical Tetrachloropyridine)	Process	Incineration	0.26/0.26	1,228.0	-	415.4	1,600,000	1,600,000
	Equipment Leak	Equipment & Work Practices	23.7/36.9	28.0	12.2	19.7	830	550
	Storage							
	- Tank 10	FR - PO	0.0/0.0	15.7	0.0	4.1	468,000	367,000
		FR - SS	0.0/0.0	17.9	0.0	4.7	121,000	95,000
		Condenser	0.3/0.4	110.8	0.1	29.0	103,000	80,500
	- Tank 11	Condenser	0.2/0.3	110.8	0.1	29.0	126,000	98,800
	- Tank 12	FR - PO	0.0/0.0	15.7	0.0	4.1	4,320,000	1,080,000
		FR - SS	0.0/0.0	17.9	0.0	4.7	446,000	111,000
		Condenser	0.1/0.4	110.8	0.1	29.0	328,000	81,900
	- Tank 13	Condenser	0.0/0.1	110.8	0.0	29.1	943,000	472,000
Dow Chemical/ Pittsburg, CA (Symmetrical Tetrachloropyridine)	Process	Incineration	0.6/0.7	1,209.0	-	411.6	732,000	622,000
	Equipment Leak	Equipment & Work Practices	4.8/16.8	31.5	5.5	16.2	3,380	970
Dow Chemical/ Midland, MI (Confidential Process 1)	Process	Incineration	9.2/10.1	1,209.0	-	459.9	50,200	45,400
	Equipment Leak	Equipment & Work Practices	27.5/50.7	25.0	16.7	1.3	50	30
Dow Chemical/ Allyn's Pt., CT (Confidenial Process 2)	Process	Incineration	0.5/99.4	1,182	-	401.6	759,000	4,040
	Equipment Leak	Equipment & Work Practices	1.4/11.3	17.7	3.7	7.6	5,060	670
Dow Chemical/ Dalton, GA (Confidential Process 2)	Process	Incineration	0.5/99.4	1,182.0	-	401.6	759,000	4,040
	Equipment Leak	Equipment & Work Practices	1.4/11.3	17.7	3.7	7.6	5,060	670
Dow Chemical/ Freeport, TX (Confidential Process 2)	Process	Incineration	0.5/99.4	1,182.0	-	401.6	759,000	4,040
	Equipment Leak	Equipment & Work Practices	1.4/11.3	17.7	3.7	7.6	5,060	670

TABLE 11-2. (Continued)

Company/Location	Emission Type/Source	Control	CCl_4/VOC Emission Reduction (Mg/yr)	Capital Cost (M$)	Recovery Credit (M$)	Net Annual Cost (M$)	Cost Effectiveness	
							CCl_4 ($/Mg)	VOC ($/Mg)
Dow Chemical/ Midland, MI (Confidential Process 2)	Process	Incineration	0.5/99.4	1,182.0	-	401.6	759,000	4,040
	Equipment Leak	Equipment & Work Practices	1.4/11.3	17.7	3.7	7.6	5,060	670
Dow Chemical/ Pittsburg, CA (Confidential Process 2)	Process	Incineration	0.5/99.4	1,182.0	-	401.6	759,000	4,040
	Equipment Leak	Equipment & Work Practices	1.4/11.3	17.7	3.7	7.6	5,060	670

Control cost effectiveness ranged from $4,040/Mg of VOC for Dow's five Confidential process 2 facilities to $1,600,000/Mg of VOC for Dow's Freeport, Texas symmetrical tetrachloropyridine process. A total emission reduction 12.6 Mg/yr of CCl_4 can be achieved by controlling the process vent emissions by incineration.

11.4.2 Control of Equipment Leak Emissions

The cost of controlling fugitive emissions for all of Dow's miscellaneous processes were estimated using control techniques required by the benzene fugitives NESHAP. The control cost effectiveness ranged from $30/Mg of VOC for confidential process 1 to $970/Mg of VOC for the symmetrical tetrachloropyridine process at Dow's plant in Pittsburg, California. A total emission reduction of 63 Mg/yr of CCl_4 can be achieved by fugitive emissions control at these facilities.

11.4.3 Control of Storage Emissions

Estimated costs for controlling all fixed roof storage tanks containing CCl_4 are presented in Table 11-2. Costs were estimated only for storage tanks at Dow's Freeport, Texas symmetrical tetrachloropyridine plant. The other facilities were already controlled and therefore did not need additional controls. Three options were costed: installation of internal floating roof with primary seals only (FR-PO), installation of internal floating roofs with primary and secondary seals (FR-SS), and a refrigerated condenser system.

The cost effectiveness of these controls ranged from $80,500/Mg of VOC using the condenser to $1,080,000/Mg of VOC using the FR-PO control option. Implementation of controls for these four tanks would reduce CCl_4 emissions by 0.6 Mg/yr.

11.5 SUMMARY OF COST-EFFECTIVENESS

Table 11-3 summarizes the estimated CCl_4 emission reductions as a function of cost effectiveness. A 53 percent (76.2 Mg/yr) reduction in CCl_4

TABLE 11-3. ESTIMATED CCl_4 EMISSION REDUCTIONS AS A FUNCTION OF COST EFFECTIVENESS

Cost Effectiveness Range ($/Mg VOC)	Nationwide CCl_4 Emission Reduction (Mg/Yr)			
	Process	Fugitive	Storage	Total
Credit	-	-	-	-
0 - 500	-	27.5	-	27.5
500 - 1,000	-	35.5	-	35.5
1,000 - 2,000	-	-	-	-
2,000 - 5,000	2.5	-	-	2.5
>5,000	10.1	-	0.6	10.7
TOTAL	12.6	63.0	0.6	76.2

emissions would result if all uncontrolled emission sources at these Dow's miscellaneous production facilities are controlled. A 44 percent emission reduction (63.0 Mg/yr) can be achieved, for less than $1,000/Mg CCl_4.

11.6 REFERENCES

1. Letter and attachments from Arnold, S. L., Dow Chemical U.S.A. to Farmer, J. R., EPA:ESED. March 1985. Response to Section 114 Letter.

2. Letter and attachments from Arnold, S. L., Dow Chemical U.S.A. to Farmer, J. R., EPA:ESED. February 26, 1985. Response to Section 114 Letter.

12.0 OTHER SOURCES OF EMISSIONS

Three additional sources of carbon tetrachloride emissions are publicly owned treatment works, bulk terminals, and distribution facilities. The available emissions information on each of these is presented in the following sections.

12.1 PUBLICLY OWNED TREATMENT WORKS

EPA studies have estimated emissions of carbon tetrachloride (CCl_4) from publicly owned treatment works (POTWs).[1] The source of these emissions is considered to be industrial discharges of waste streams containing CCl_4. The studies have estimated that up to 220 Mg of CCl_4 is emitted annually from a set of 1,600 POTWs known to handle industrial discharges. Recent ambient air monitoring around the Philadelphia POTW indicates that these estimates may overstate CCl_4 emissions by up to a factor of 10.

12.2 BULK TERMINALS

Bulk terminals operations are a source of carbon tetrachloride storage and handling emissions. A recent study on CCl_4 emissions identified two bulk terminal facilities with reported emissions of 1 Mg/yr from a 1980 Texas emission inventory.[2] One tank at GATX Terminal Corp. and one loading operation at PAK Tank Gulf Coast Inc. were each cited as having 1 Mg/yr CCl_4 emissions.

Tanks used to store chlorinated solvents in bulk terminals range in size from about 40,000 gallons to 200,000 gallons. Turnover frequency ranges from 1 to 6 turnovers per year and average about 2.5 per year for chemical storage.[3] Bulk storage tanks are often switched from one chemical to another over the period of one year depending on the length of contracts.

12.3 DISTRIBUTION FACILITIES

Distribution facilities are also a potential source of CCl_4 storage and handling emissions. About 731 Mg of CCl_4 was sold through distributors in 1983. The distributor typically buys CCl_4 in tank truck quantities and packages it in 55 gallon drums or smaller containers. This operation may require storage prior to drumming which may result in storage emissions. Emissions also result from vapor displacement in the filling of drums and other containers. Based on the total quantity handled by distributors and AP-42 methods for estimating loading emissions, total emissions from all distribution facilities are estimated to be less than 9 Mg/yr.

Several large distributors were contacted to identify those handling CCl_4. Only one CCl_4 distributor, McKesson Chemical Company, was identified. McKesson receives a tank car of CCl_4 once or twice a year that is drummed directly from the tank car. There are no storage tanks for CCl_4.[4]

12.4 REFERENCES

1. Memorandum and attachments from Lahre, T., EPA:AMTB, to Southerland, J. H., EPA:AMTB. December 5, 1983. Initial look at available emissions data on POTWs.

2. Smith, M.G. (GCA Corporation.) Preliminary Study of Sources of Carbon Tetrachloride. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. EPA Contract No. 68-02-3510. June 1983. p. 10-7.

3. Telecon. Mesavage, C., International Liquid Terminals Association, with Howle, R. H., Radian Corporation. February 26, 1985. Conversation about storage of chlorinated solvents.

4. Telecon. Eisner, D., McKesson Chemical Company., with Howle, R. H., Radian Corporation. February 7, 1985. Conversation about storage of chlorinated solvents.

APPENDIX A

PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE

TABLE A-1. PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE, CCl_4

Property	Value
Synonyms: Tetrachloromethane, methane tetrachloride, perchloromethane, benzinoform	
CAS Registry No.	56-23-5
Molecular weight	153.82
Melting point, °C	-22.92
Boiling point, °C	76.72
Specific gravity	
20/4°C	1.59472
Autoignition temperature, °C	>1,000
Flash point, °C	None
Vapor density, air = 1	5.32
Critical temperature, °C	283.2
Critical pressure, MPa	4.6
Thermal conductivity, mW/(m•K)	
Liquid, 20°C	118
Vapor, bp	7.29
Average coefficient of volume expansion, 0 - 40°C	0.00124
Heat of combustion, liquid, at constant volume, 18.7°C, kJ/mol	365
Viscosity, 20°C, mPa s	0.965

TABLE A-1. (Continued)

Property	Value
Vapor pressure, kPa	
C°C	4.410
20°C	11.94
40°C	28.12
60°C	58.53
150°C	607.3
200°C	1,458
Solubility of CCl_4 in water, 25°C g/100 g H_2O	0.08
Solubility of water in CCl_4, 25°C, g/100 g CCl_4	0.013
Liquid specific gravity	1.61

APPENDIX B

METHODS USED FOR ESTIMATING STORAGE TANK AND EQUIPMENT LEAK EMISSIONS

APPENDIX B

METHODS USED FOR ESTIMATING STORAGE TANKS AND EQUIPMENT LEAK EMISSIONS

B.1 EMISSION FACTORS FOR FIXED-ROOF STORAGE TANKS

B.1.1 Emission Equations

The major types of emissions from fixed-roof storage tanks are breathing and working losses. Emission equations for breathing and working losses from storage tanks were developed in EPA Publication No. AP-42. The equations used in estimating emissions rates for fixed-roof tanks storing VOL are:

- $L_T = L_B + L_W$
- $L_B = 1.02 \times 10^{-5} M_v \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.5} F_p C K_c$
- $L_W = 1.09 \times 10^{-8} M_v P V N K_n K_c$

where, L_T = total loss (Mg/yr)
L_B = breathing loss (Mg/yr)
L_W = working loss (Mg/yr)

B.1.2 Parameter Values and Assumptions

The following CCl_4 physical property values, plant-specific information, and engineering assumptions were used to estimate the emission losses:

M_v = molecular weight of product vapor (lb/lb mole);
for CCl_4, $M_v = 153.82$
P = true vapor pressure of product, 1.80 psia
D = tank diameter (ft); dependent upon plant-specific information.
C = tank diameter factor (dimensionless):
for diameter $\geq$ 30 feet, C = 1
for diameter < 30 feet, $C = 0.0771\,D - 0.0013(D)^2 - 0.1334$
V = tank capacity (gal); dependent upon plant-specific information

N = number of turnovers per year (dimensionless); dependent upon plant-specific information

T = average diurnal temperature change in °F; 20°F was assumed for the storage tanks at these facilities

F_p = paint factor (dimensionless); the storage tanks were assumed to be in good condition and painted white; therefore, $F_p = 1$ (see Table B-1)

H = average vapor space height (ft): used tank-specific values or an assumed value of one-half the tank height (H/2)

K_c = product factor (dimensionless) = 1.0 for VOL

K_n = turnover factor (dimensionless); dependent upon plant-specific information

for turnovers > 36, $K_n = \frac{180 + N}{6N}$

for turnovers $\leqq$ 36, $K_n = 1$

B.1.3 Sample Calculation

The following sample calculation is provided to demonstrate the evaluation of emissions from a typical fixed-roof storage tank containing CCl_4. For the general equations,

$$L_T = L_w + L_B$$

$$L_B = 1.02 \times 10^{-5}\ M_v \left(\frac{P}{14.7-P}\right)^{0.68} D^{\,1.73}\ H^{\,0.51}\ T^{\,0.5}\ F_p C K_C$$

$$L_w = 1.09 \times 10^{-8}\ M_v\ PVNK_n K_C$$

where, M_v = 153.82

P = 1.80 psia

D = 37 ft

C = 1

V = 233,000 gallons

N = 10

T = 20°F

F_p = 1.0

H = 14 ft

K_C = 1.0

K_n = 1

TABLE B-1. PAINT FACTORS FOR FIXED-ROOF TANKS[1]

Tank Color		Paint factors (F_p) Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44
Medium gray	Medium gray	1.40	1.58

The emissions from this storage tank are:

$$L_B = 1.02 \times 10^{-5}\ (153.82)\left[\frac{1.8}{14.7-1.8}\right]^{0.68}(37)^{1.73}(14)^{0.51}(20)^{0.5}(1)(1)(1)$$

$$= 3.648\ \text{Mg/yr}$$

$$L_W = 1.09 \times 10^{-8}\ (153.82)(1.8)(233{,}000)(10)(1)(1)$$

$$= 7.032\ \text{Mg/yr}$$

$$L_T = 3.648\ \text{Mg/yr} + 7.032\ \text{Mg/yr} = 10.68\ \text{Mg/yr}$$

B.2 EMISSION FACTORS FOR INTERNAL FLOATING ROOF STORAGE TANKS

B.2.1 Emission Equations

Emissions from internal floating roof tanks can be estimated from the following equations:[1] (Note that these equations apply only to freely vented internal floating roof tanks.)

$$L_T = L_W + L_r + L_f + L_d$$

where, L_T = the total loss (Mg/yr)

L_W = the working loss (Mg/yr) = $\frac{(0.943)\ Q\ C\ W_L}{D}\quad 1 + \frac{N_C F_C}{D}\quad /2205$

where, D = tank diameter (ft)

N_C = number of columns (dimensionless); (see Table B-2)

F_C = effective column diameter (ft); 1.0 assumed

L_r = the rim seal loss (Mg/yr) = $(K_r D)\ P^*\ M_V\ K_C/2205$

L_f = the fitting loss (Mg/yr) = $(F_f)\ P^*\ M_V\ K_C/2205$

L_d = the deck seam loss (Mg/yr) = $(F_d\ K_d\ D^2)\ P^*\ M_V\ K_C/2205$

B.2.2 Parameter Values and Assumptions

The assumptions and values used to calculate emissions from internal floating roof tanks are:

Q = product average throughput (bbl/yr); tank capacity (bbl/turnover) x turnovers/yr; dependent upon plant-specific information

C = product withdrawal shell clingage factor (bbl/10^3 ft^2); use 0.0015 bbl/$10^3 ft^2$ for VOL in a welded steel tank with light rust (0.0075 for dense rust)

W_L = density of product (lb/gal); for CCl_4, 13.4 lb/gal

D = tank diameter (ft)

N_c = number of columns (dimensionless); (see Table B-2)

F_c = effective column diameter (ft); 1.0 assumed

D = the tank diameter (ft); dependent upon plant-specific information

M_v = the average molecular weight of the product vapor (lb/lb mole). For CCl_4, $M_v = 153.82$

K_C = the product factor (dimensionless) = 1.0 for VOL

2205 = constant (lb/Mg)

P^* = the vapor pressure function (dimensionless)

$P^* = 0.068\ P/((1 + (1 - 0.068\ P)^{0.5})^2)$

P = the true vapor pressure of the material stored (1.8 psia for CCl_4)

K_r = the rim seal loss factor (lb mole/ft yr) that for an average fitting seal is as follows:

Seal system description	K_r (lb mole/ft yr)
Vapor-mounted primary seal only	6.7
Liquid-mounted primary seal only	3.0
Vapor-mounted primary seal plus secondary seal	2.5
Liquid-mounted primary seal plus secondary seal	1.6

F_f = the total deck fitting loss factor (lb mole/yr)

$$= \sum_{i=1}^{n} (N_{f_i} K_{f_i}) = [(N_{f_1} K_{f_1}) + (N_{f_2} K_{f_2}) + \ldots + (N_{f_n} K_{f_n})]$$

TABLE B-2. TYPICAL NUMBER OF COLUMNS AS A FUNCTION OF TANK DIAMETERS

Tank Diameter Range D (Ft)			
Greater Than	And	Less Than Or Equal To	Typical Number Columns, N_C
0		85	1
85		100	6
100		120	7
120		135	8
135		150	9
150		170	16
170		190	19
190		220	22
220		235	31
235		270	37
270		275	43
275		290	49
290		330	61
330		360	71
360		400	81

where, N_{f_i} = number of fittings of a particular type (dimensionless). N_{f_i} is determined for the specific tank or estimated from Tables B-2 and B-3. The values used for these emissions estimates are designated by * in Table B-3.

K_{f_i} = deck fitting loss factor for a particular type fitting (lb mole/yr). K_{f_i} is determined for each fitting type from Table B-3. The values used for these emissions estimates are designated by *.

n = number of different types of fittings (dimensionless)

F_d = the deck seam length factor (ft/ft²)

= 0.15, for a deck constructed from continuous metal sheets with a 7 ft spacing between seams

= 0.33, for a deck constructed from rectangular panels 5 ft by 7.5 ft

= 0.20, an approximate value for use when no construction details are known

K_d = the deck seam loss factor (lb mole/ft yr)

= 0.34 for nonwelded roofs

= 0 for welded decks

B.2.3 Sample Calculation

The following sample calculation is provided to demonstrate the evaluation of emissions from a typical storage tank with an internal floating roof containing CCl_4. For the general equations,

$$L_T = L_w + L_r + L_f + L_d \cdot$$

$$L_w = \frac{(0.943)QCW_L}{D}\left[1 + \frac{N_c F_c}{D}\right]/2205$$

$$L_r = (K_r D)\ P^*\ M_V\ K_c/2205$$

Table B-3 SUMMARY OF DECK FITTING LOSS FACTORS (K_f) AND TYPICAL NUMBER OF FITTINGS (N_f)

Deck fitting type	Deck fitting loss factor, K_f (lbmole/yr)	Typical number of fittings, (N_f)
1. Access Hatch		1
a. Bolted cover, gasketed	1.6	
b. Unbolted cover, gasketed	11	
c. Unbolted cover, ungasketed	25	
2. Automatic Gauge Float Well		1
a. Bolted cover, gasketed	5.1	
b. Unbolted cover, gasketed	15	
c. Unbolted cover, ungasketed	28	
3. Column Well		(see Table B-2)
a. Built-up column-sliding cover, gasketed	33	
b. Built-up column-sliding cover, ungasketed	47	
c. Pipe column-flexible fabric sleeve seal	10	
d. Pipe column-sliding cover, gasketed	19	
e. Pipe column-sliding cover, ungasketed	32	
4. Ladder Well		1
a. Sliding cover, gasketed	56	
b. Sliding cover, ungasketed	76	
5. Roof Leg or Hanger Well		$(5 + \frac{D}{10} + \frac{D^2}{600})$[a]
a. Adjustable	7.9	
b. Fixed	0	
6. Sample Pipe or Well		1
a. Slotted pipe-sliding cover, gasketed	44	
b. Slotted pipe-sliding cover, ungasketed	57	
c. Sample well-slit fabric seal, 10% open area	12	
7. Stub Drain*, 1-inch diameter	1.2	$(\frac{D^2}{125})$[b]
8. Vacuum Breaker		1
a. Weighted mechanical actuation, gasketed	0.7	
b. Weighted mechanical actuation, ungasketed	0.9	

[a] Not used on welded, contact internal floating decks.

[b] D = tank diameter (ft).

* Values used for estimating internal floating roof storage tank emissions

$L_f = (F_f)\ P^*\ M_v\ K_c/2205$

$L_d = (F_d K_d D^2)\ P^*\ M_v\ K_c/2205$

where, M_v = 153.82 lb/lb mole

P^* = 0.0326

Q = 500,000 bbl/yr

C = 0.0015

W_L = 13.4 lb/gal

D = 30 ft

N_c = 1

F_c = 1.0

K_r = 6.7 lb mole/ft yr

K_c = 1.0

F_f = 242 lb mole yr

F_d = 0.20

K_d = 0

The emissions from this storage tank are:

$$L_W = \left[\frac{(0.943)(500{,}000)(0.0015)(13.4)}{30} \quad \left(1 + \frac{(1)(1)}{30}\right)\right]/2205$$

$$= 0.148 \text{ Mg/yr}$$

$$L_r = ((6.7)(30))(0.0326)(153.82)(1.0)/2205$$

$$= 0.457 \text{ Mg/yr}$$

$$L_f = (242)(0.0326)(153.82)(1.0)/2205$$

$$= 0.550 \text{ Mg/yr}$$

$$L_d = ((0.20)(0.34)(30)^2)(0.0326)(153.82)(1.0)/2205$$

$$= 0.139 \text{ Mg/yr}$$

$$L_T = 0.148 \text{ Mg/yr} + 0.457 \text{ Mg/yr} + 0.550 \text{ Mg/yr} + 0.139 \text{ Mg/yr}$$

$$L_T = 1.3 \text{ Mg/yr}$$

B.3 EQUIPMENT LEAK EMISSIONS - SAMPLE CALCULATIONS

Emissions were estimated from the number of equipment leak sources (provided by the plant), the percentage of CCl_4 in the stream (provided by the plant), and the emission factors for each type of equipment (from the SOCMI AID).[2] The following sample calculations illustrate the procedure.

Emissions Source	Number		% CCl_4 Service		kg/hr/source Emission Factor[a]		Total Emissions kg/hr
Pump seals	3	x	7.5	x	0.0494	=	0.011
	6	x	50.5	x	0.0494	=	0.150
	2	x	87.5	x	0.0494	=	0.086
	12	x	100.0	x	0.0494	=	0.593

Emissions Source	Number		% CCl_4 Service		kg/hr/source Emission Factor[a]		Total Emissions kg/hr
Compressors	1	x	87.5	x	0.228	=	0.200
Flanges	4	x	5.0	x	0.00083	=	0.0002
	112	x	7.5	x	0.00083	=	0.007
	30	x	18.0	x	0.00083	=	0.004
	235	x	50.5	x	0.00083	=	0.099
	66	x	87.5	x	0.00083	=	0.048
	456	x	100.0	x	0.00083	=	0.378
Valves (gas)	4	x	5.0	x	0.0056	=	0.001
	8	x	7.5	x	0.0056	=	0.003
	3	x	50.5	x	0.0056	=	0.008
	4	x	87.5	x	0.0056	=	0.020
	11	x	100.0	x	0.0056	=	0.062
Valves (liquid)	5	x	5.0	x	0.0071	=	0.002
	3	x	7.5	x	0.0071	=	0.002
	8	x	87.5	x	0.0071	=	0.050
	9	x	100.0	x	0.0071	=	0.064
Pressure Relief Devices	2	x	5.0	x	0.1042	=	0.01
	4	x	50.5	x	0.1042	=	0.21
	6	x	100.0	x	0.1042	=	0.63
Sampling Connections	5	x	5.0	x	0.0150	=	0.004
	3	x	50.5	x	0.0150	=	0.023
	1	x	87.5	x	0.0150	=	0.013
	3	x	100.0	x	0.0150	=	0.045
Open Ended Lines	1	x	100.0	x	0.0017	=	0.002
					TOTAL	=	2.7252

$$\text{Annual Emissions} = 2.72\ \text{kg/hr} \times 8760\ \frac{\text{hrs}}{\text{year}} \times \frac{\text{Mg}}{1{,}000\ \text{kg}}$$

$$= 23.87\ \text{Mg}$$

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[a] U. S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions, and Costs. Research Triangle Park, NC. Publication No. EPA-450/3-82-010. April 1982.

B.4 REFERENCES

1. U. S. Environmental Protection Agency. VOC Emissions from Volatile Organic Liquid Storage Tanks - Background Information for Proposed Standards. Research Triangle Park, North Carolina. Publication No. EPA-450/3-81-003a. July 1984. 252 pp.

2. U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information on Emissions, Emission Reductions, and Costs. Research Triangle Park, N.C. Publication No. EPA-450/3-82-010. April 1982.

APPENDIX C
METHODS FOR ESTIMATING EMISSION CONTROL COSTS

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METHODS FOR ESTIMATING EMISSION CONTROL COSTS

C.1 PROCESS VENT EMISSIONS CONTROL COST ESTIMATION

The cost estimates for process vent emission control are based on the use of thermal incineration. The procedure for estimating these costs uses the methods presented in the Air Oxidation Processes Control Techniques Guidelines (CTG) document for estimating the cost of controlling VOC emissions through incineration.[1] A detailed discussion of the incinerator costing methods may be found in Chapter 5 of the Air Oxidation CTG document.

The total installed capital cost of control is determined using the following equation:

Total Installed Capital Cost (10^3\$) = (# of incinerators) x (deescalation factor) x (C1 - (Waste Heat Boiler Correction Factor) + (C2 x (Flowrate per incinerator ÷ Design Vent Size Factor)^{C3}) + (pipe rack cost) + (additional ductwork cost)

where: C1, C2, and C3 are coefficients from Table C-1 that depend upon heating value and halogenation status of a given vent stream; waste heat boiler correction factor of 40 (10^3\$) is used for vent streams with flowrates below 700 scfm, where no heat recovery in a waste heat boiler is assumed; deescalation factor of 0.90 deescalates costs to 1978 dollars;

design vent size factor of 0.95 increases vent stream flowrate for costing purposes;

pipe rack cost is calculated using the equation presented in Table C-2;

additional ductwork cost is calculated using the equation presented in Table C-3.

A sample calculation for incinerator costing is shown in Table C-6. The calculation is based on vent stream parameters obtained from the Stauffer Chemical Company (Le Moyne, Alabama) Section 114 letter response. The cost estimate was initially calculated in 1978 dollars and then was updated to 1984 dollars using the annualized cost escalation factor shown in Table C-7.

TABLE C-1. TOTAL INSTALLED CAPITAL COST AS A FUNCTION OF VENT STREAM FLOW RATE

Category	Maximum Flowrate Per Unit (10^3 scm/min)	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Fabricated Equipment Cost Escalation Factor	C1	C2	C3
A1[a]	0.74	0.0	3.5	0.90	803.11	12.83	0.88
A2[a]	0.74	3.5	-	0.90	786.61	12.44	0.88
B	1.42	0.0	0.48	0.90	259.88	4.91	0.88
C	1.42	0.48	1.9	0.90	297.99	2.84	0.88
D	1.25	1.9	3.6	0.90	236.35	3.23	0.88
E[a]	1.25	3.6	-	0.90	236.35	3.23	0.88

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[a] Halogenated vent stream.

[b] Dilution flow rate is used in capital cost equation. Dilution flow rate = (design flow rate) x (original heating value) ÷ (3.65 MJ/scm).

TABLE C-2. ADDITIONAL DUCT COST[1,2]

Additional duct cost (10^3 \$) = (length) x (cost per unit length) x (installation factor) x (duct deescalation factor) x (retrofit correction factor) ÷ 1000

Cost per unit length = 1.37L - 1.76

where L = duct diameter in inches

$$\text{Diameter} = \left[\frac{\text{Flow rate (ft}^3\text{/min)}}{\text{Linear velocity (ft/min)}} \times \frac{4}{\pi} \right]^{\frac{1}{2}}$$

$$= \left[\frac{\text{Flow rate (ft}^3\text{/min)}}{2000 \text{ ft/min}} \times \frac{4}{3.1412} \right]^{0.5}$$

if linear velocity is assumed to be 2000 ft/min

Additional duct length = 150 ft + (additional vents x 100 ft/vent)

Installation factor = 1.087

Escalation factor (from 1977 to 1978) = 1.088

Retrofit correction factor = 1.0

TABLE C-3. PIPE RACK COST[1,2]

Pipe rack cost (10^3 \$) = (pipe rack length) x (cost per unit length) x (installation factor) x (pipe rack deescalation factor) x (retrofit correction factor) ÷ 1000

Pipe rack length = 250 ft + (# additional vents x 100 ft/vent)

Cost per unit length = \$32.045/ft

Installation factor = 1.087

Deescalation factor (1982 to 1978) = 0.746

Retrofit correction factor = 1.0

TABLE C-4. OPERATING FACTORS FOR EACH DESIGN CATEGORY

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Ratio of Flue Gas Flow to Offgas Flow[a]	Heat Recovery Factor (MJ/scm)	Pressure Drop (Inches H_2O)	Natural Gas Use Coefficients			
						G0	G1	G2	G3
A1[b]	0	3.5	2.9	3.38	22[c]	0	4.56	-0.985	0
A2[b]	3.5	-	2.9	3.38	22[c]	0	0.329	0	0
B	0.	0.48	1.9	0	10[d]	0.425	0.666	-1.29	0.015
C	0.48	1.9	2.3	0	10[d]	0	2.39	-1.22	0
D	1.9	3.6	2.5	0	6[e]	0	0.183	0	0
E	3.6	-	2.5	0	6[e]	0	0.183	0	0

[a] Both at standard conditions.

[b] Offgas contains halogenated compounds.

[c] Includes 6 inches across the combustion chamber, 4 inches across the waste heat boiler, and 12 inches across the scrubber.

[d] Includes 6 inches across the combustion chamber and 4 inches across the recuperative heat exchanger.

[e] Across the combustion chamber.

TABLE C-5. ANNUALIZED COST FACTORS

All Factors are Based on June 1980

Direct

Operating Labor: \$8.50/hr

Operating Labor Factor:

- 2400 Man-hr/yr (Categories A1-A2)
- 2133 Man-hr/yr (Categories B-C)
- 1200 Man-hr/yr (Categories D-E)

Supervisory Labor: \$8.50/hr x (0.15)

Total Labor: [(\$8.50/hr x 1.15) + (0.03 of Total Installed Capital)]

Overhead Labor: 0.80 of Total Labor
Electricity: \$0.0279/kWh
Natural Gas: \$4.16/GJ =
Heat Recovery Credit: \$4.16/GJ =
Quench Water Price: \$0.22/Thousand Gallons
Scrubbing Water Price: \$0.22/Thousand Gallons
Caustic Price: \$0.0436/lb[a]
Maintenance Labor Plus Materials Factor = 0.06 of Total Installed Capital

Indirect ("Capital Charges")

Interest Rate = i = 10%

Incinerator Lifetime = 10 Years = N

$$\text{Capital Recovery Factor} = \frac{i\,(1 + i)^N}{(1 + i)^N - 1}$$

= 0.163 of Total Installed Capital

Taxes, Insurance and Administrative Charges Factor = 0.04 of Total Installed Capital

Overall Capital Charges Factor = 0.203 of Total Installed Capital

Overall Taxes and Maintenance Factor = 0.10 of Total Installed Capital

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[a] Fifty percent liquid solution of caustic soda.

[b] Memo to Hurley, E., EEA, from Galloway, J., EEA. January 13, 1981. Average capacity utilization for the air oxidation industry.

TABLE C-6. SAMPLE CALCULATION FOR INCINERATOR COSTING

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1. Capital Cost (10^{3} \$) = (# incinerators) x (incinerator capital cost per unit) x (escalation factor)
= (# incinerators) x (803.11 - 40.0 + 12.83 x $(\text{flow}/0.95)^{0.88}$) x escalation factor
= 1 x (803.11 - 40.0 + 12.83 $(14.2)^{0.88}$) x 0.9
= 806.1

2. Additional Duct Cost (10^{3} \$) = (length) x (cost per unit length) x (escalation factor) x (installation factor) = 350 ft. x $(((500)\ \text{ft}^{3}/\text{min}) \times 4 \times 2000 \times 3.1412))^{0.5}$ x 12 x 1.37 - 1.76) x 1.088 x 1.087 ÷ 1000
= 3.111

3. Pipe Rack Cost (10^{3} \$) = (length) x (cost per unit length) x (installation factor) x (pipe rack deescalation factor) x (retrofit correction factor) ÷ 1000 = 250 ft. + (# additional vents x 100 ft./vent) x \$32.045/ft. x 1.087 x 0.746 x ÷ 1000
= 11.693

4. Total Installed Total Capital = Capital cost (10^{3} \$) + extra duct cost (10^{3} \$) + pipe rack cost (10^{3} \$)
= 806.1 + 3.657 + 19.00
= 820.9

(continued)

TABLE C-6. (Continued)

5. Natural Gas Use (MJ/yr)	= (minutes per year) x (supplemental gas required per minute) = 0.5256 10^6 min/yr x G_0 + flow x ($G_1 + G_2 \times H_T$) = 0.5256 10^6 min/yr x (3.96) x (4.53 - 0.985 x 1.49) MJ/min) = 6.37 MJ/yr
6. Natural Gas Cost (10^3 \$)	= Natural gas price (\$/10^9 J) x natural gas use (MJ/yr) = \$4.16/GJ x 6.37 MJ = 26.2
7. Operating Labor Cost (10^3 \$)	= Wage (\$/hr) x labor factor (hr/yr) ÷ 1000 = \$8.50/hr x 2400 hrs = 20.4
8. Supervisory Labor Cost (10^3 \$)	= Operating labor cost (10^3/yr) x 0.15 = 20.4 (10^3 \$/yr) x 0.15 = 3.06
9. Maintenance Labor Cost (10^3 \$)	= Installed capital cost (10^3 \$) x 0.03 = 820.9 (10^3) \$ x 0.03 = 24.63
10. Overhead Labor Cost (10^3 \$)	= Operating labor cost (10^3 \$) + supervisory labor cost (10^3 \$) + maintenance labor cost (10^3 \$) x 0.80 = (20.40 + 3.06 + 24.63) x 0.80 = 38.47

(continued)

TABLE C-6. (Continued)

11. Total Labor Cost $(10^3\ \$)$ = Operating labor cost $(10^3\ \$)$ + supervisory labor cost $(10^3\ \$)$ + maintenance labor cost $(10^3\ \$)$ + overhead labor cost $(10^3\ \$)$
= 20.4 + 3.06 + 24.63 + 38.47
= 86.56

12. Electricity Cost $(10^3\ \$)$ = (electricity price) x (pressure drop) x (flow rate) x (flue gas:offgas ratio) x (fan equation conversion factor) x (# of hours per year) ÷ fan efficiency ÷ 1000
= 0.0279 (\$/KWhr) x 22 in. x 3.96 scm/min x 2.9 x 0.004136 (KW/scmin.) ÷ 0.6 ÷ 1000 $(\$/10^3\ \$)$
= 0.426

13. Quench Water Cost $(10^3\ \$)$ = (quench water price) x (flow rate) x (flue gas:offgas ratio) x (water required per unit flow) x (minutes per year) ÷ 1000
= 0.22 $(\$\ 10^3$ gal) x 3.96 (scm/min) x 2.9 x 1.68 x 10^{-5} $(10^3$ gal/scm) x 0.5256 $(10^6$ min/yr) ÷ 1000 $(\$/10^3\ \$)$
= 0.0223

(continued)

TABLE C-6. (Continued)

14. Scrubbing Water Cost (10^3 \$)	= (scrub water price) x (flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (water required per unit chlorine) x (# of hours per year) = 0.22 ($\$10^3$ gal) x 3.96 (scm/min) x 35.314 scf/scm x 2.9 x 0.0487 (lb/hr chlorine)/(scf/min flue gas) x 0.0192 (10^3 gal/lb chlorine) x 8760 (hr/yr) ÷ 1000 = 0.73
15. Neutralization Cost (10^3 \$)	= (caustic cost) x (flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (caustic requirement per unit chlorine) x (# of hours per year) ÷ 1000 = 0.0436 (\$/lb NaOH) x 3.96 (scm/min) x 35.314 scf/scm x 2.9 x 0.0487 (lb/hr chlorine)/(scf/min flue gas) x 1.14 (lb NaOH/lb chlorine) x 8760 (hr/yr) ÷ 1000 $\$/10^3$ \$ = 8.6
16. Heat Recovery Credit	= 0 (for all streams <700 scfm)

(continued)

TABLE C-6. (Continued)

17. Taxes, Insurance, and Maintenance Cost (10^3 \$)
= (installed capital cost) x (taxes, insurance, and administrative charges factor + maintenance labor factor)
= 820.9 (10^3 \$) x (0.04 + 0.03)
= 57.46

18. Annual Operating Cost (10^3 \$)
= (TI&M cost) + (gas cost) + total labor cost) + (electricity cost) + (quench cost) + (scrubbing cost) + (scrubbing cost) + (caustic cost)
= 57.46 + 26.20 + 86.56 + 0.426 + 0.0223 + 0.73 + 8.6
= 180.0

19. Annualized Cost (10^3 \$)
= (operating cost) + (capital recovery factor x total installed capital cost)
= 180.0 + (.163 x 820.9)
= 313.8

20. Annual Emissions (Mg/yr)
= (hourly emissions) x 365 (days/yr) x 24 (hrs/day) x (Mg/10^3 kg)
= 15.86 kg/hr x 365 (days/yr) x 24 (hrs/day) x 1 (Mg/10^3 kg)
= 138.9

21. Annual Emission Reduction (Mg/yr)
= (annual emissions) x 0.98
= 138.9 x 0.98 (CCl_4) = 136.1 (CCl_4)
= 349.6 (VOC)

(continued)

TABLE C-6. (Continued)

22. Cost Effectiveness (\$/Mg)	= (annual cost) ÷ (annual emission reduction) = 313.8 (10^3 \$) ÷ 136.1 Mg (CCl_4) = 2305/Mg (CCl_4) = 313.8 (10^3 \$) ÷ 349.6 Mg (VOC) = 898/Mg
23. Updated Cost-Effectiveness Values (\$/Mg)	= 2305 (\$/Mg) x 1.486 = \$3420/Mg (CCl_4) = 898 (\$/Mg) x 1.486 = \$1330/Mg (VOC)

TABLE C-7. COST CONVERSION FACTORS

Original Cost Component	Conversion Year	Factor
Incinerator	1979	0.900
Pipe Rack	1982	0.745
Duct Work	1977	1.088
Annualized Costs	1978	1.486

C.2 SAMPLE COST CALCULATIONS FOR CONTROL OF PROCESS EMISSIONS USING CARBON ADSORBERS

Data and calculations presented are for determining the capital costs, annual costs, and cost effectiveness of carbon adsorption. The total installed capital cost is a function of the amount of carbon needed to adsorb carbon tetrachloride (CCl_4). The adsorption isotherms for CCl_4 shows that 0.1 lbs of CCl_4 is absorbed per pound of carbon. The carbon absorber is estimated to be 95% efficient.

Diamond Shamrock's Delaware City, DE chlorine production facility will be used as an example to calculate the cost effectiveness of CCl_4 removal by carbon adsorption. (CCl_4 emission rate = 22.6 lb/hr, max vent rate = 68.5 scfm, and capacity utilization rate = 0.80)

AMOUNT OF CARBON NEEDED =

$$\frac{22.6 \text{ lb/Hr} \times 1 \text{ Hr}}{0.1 \text{ lb/lb Carbon}} = 226 \text{ lbs}$$

As the carbon reaches capacity, it will have to be regenerated. Therefore, an additional carbon bed is needed for use when one bed is being regenerated.

TOTAL CARBON REQUIRED = 2 x 226 lbs = 452 lbs.

C.2.1 Capital Cost

Cost curves developed by Gard, Inc. for the EPA were used to estimate capital cost.[2] The cost of $22,500 (Dec. 1977) includes the adsorber, carbon, blower or fan, controls and steam generator. As there will be chlorine present in the gas stream, precautions for corrosion must be taken. Therefore, a stainless steel carbon adsorber is recommended. A cost increase of 2.3 times is estimated.[2]

$22,500 x 2.3 = $51,750

Also, taxes, shipping, and installation costs must be included. A cost increase of 1.75 times is estimated.[3]

$$\$51,750 \times 1.75 = \$90,562$$

Finally, the capital costs were updated to November 1984 using Chemical Engineering Cost Index for Fabricated Equipment.

$$\$90,562 \times \frac{335.4 \text{ (Nov. 1984)}}{226.2 \text{ (Dec. 1977)}} = \$134,300$$

The fabricated equipment cost factor is used to simplify the updating of the capital and annualized costs.

C.2.2 Annual Cost

The annualized cost is based on 5800 hours of operation. The calculations for operating labor, maintenance, carbon replacement, steam for regeneration, electricity, and cooling water are presented below. The operating labor ($15.00/hr) is for control device operation and is only 360 man-hours per year. The maintenance factor is 0.05 of the total capital cost. Indirect capital charges such as interest (10 percent), taxes, insurance, and administrative charges are all grouped together under capital charges at 22 percent of the total installed capital cost.[3]

- Operating labor ($15.00/hr):

  $$(\$15.00/\text{hr})(360 \text{ manhours}) = \$5,400$$

- Maintenance labor plus materials factor (0.05 of total installed capital cost):

  $$0.05 \times \$134,300 = \$6,715$$

- Carbon replacement (estimated to be every 5 years):

  $$\frac{452 \text{ lbs}}{5 \text{ yrs}} \times \$1.75/\text{lb} = \$158$$

- Steam for regenerating carbon ($\frac{\$5.04}{1000\text{ lbs}}$):

$$22.6\ \frac{\text{lbs CCl}_4}{\text{Hr}} \times 5800\text{ hrs} \times 4\ \frac{\text{lb steam}}{\text{lb VOC}} \times \frac{\$5.04}{1000\text{ lb steam}} = \$2{,}643$$

- Electricity (\$0.0506/kwh):

$$68.5\text{ cfm} \times \frac{5\text{ hp}}{1000\text{ cfm}} \times \frac{0.746\text{ kwh}}{\text{hph}} \times 5800\text{ hr} \times \$0.0506/\text{kwh} = \$75$$

- Cooling Water (\$0.22/1000 gallons):

$$\frac{12\text{ gal}}{100\text{ lb steam}} \times \frac{90.4\text{ lb steam}}{\text{hr}} \times 5800\text{ hr} \times \frac{\$0.22}{1000\text{ gal}} = \$14$$

- Capital Charges (22 percent of installed capital cost):

  0.22 x 134,300 = \$29,546

The total operating costs are \$44,550/yr. There is a recovery credit of \$330/Mg of CCl_4 which is recovered for reuse.

Annual emissions reduction with carbon adsorber:

89.811 x 0.95 = 85.3 Mg/yr

Recovery Credit = \$330/Mg x 85.3 Mg/yr = \$28,150

Therefore, the total annualized cost equals

\$44,550 - \$28,150 = \$16,400

Cost effectiveness = \$16,400 ÷ 85.3 Mg/yr

= \$200/Mg

C.3 COST CALCULATIONS FOR INSTALLING INTERNAL FLOATING ROOFS IN FIXED ROOF TANKS

The following equations were used to calculate the capital and annualized cost for the installation of a mild steel welded contact internal floating roof to a fixed roof storge tank. This internal floating roof utilizes both primary (constructed of Teflon^R) and secondary (constructed of Viton^R) seals.

C.3.1 Capital Cost (4th Quarter 1982 Dollars)

1. Degassing Cost[4]

Cost = \$130.8 $V^{0.5132}$ or \$1,000, whichever is greater where V = tank volume in cubic meters.

2. Estimated Installation Cost[4]

a. Basic cost of roof and primary seal:
Cost = (1.91 + 2.54 x D) x \$1,000 + (\$204 x D)
D = tank diameter in meters

(The \$204 x D cost reflects the additional cost of using Teflon^R coated fiberglass versus the standard polyurethane coating)[5]

b. Additional cost of adding secondary seal:[4]

Cost = \$580 x D

(The \$580 x D cost reflects using a Viton^R coating material for the secondary seal)

3. Door Sheet Opening Cost[6]

Cost = \$1,300

Total capital cost (primary seal) = degassing cost + estimated installed cost (2a) + door sheet opening cost.

Total capital cost (primary + secondary seals) = degassing costs + estimated installed cost (2a,b) + door sheet opening cost.

C.3.2 Annual Cost (4th Quarter 1982 Dollars)

1. Tax, insurance, and administration -- 4% of capital cost (based on 10 percent interest rate and 10 year equipment life)

2. Maintenance -- 5% of capital cost

3. Inspection -- 1% of capital cost

4. Capital recovery factor -- 16.275% of capital cost

Total annual cost = [26.275% of capital cost]

C.3.3 CCl_4/VOC Reduction

1. Emissions calculated for fixed roof tanks using AP-42 formulas.

2. Emissions calculated for internal floating roof tanks using AP-42 formulas.
   a. Liquid mounted primary seal only
   b. Liquid primary and secondary seal

3. Emissions from fixed roof tank - emissions from internal floating roof tank = VOC emission reduction

   CCl_4 emission reduction = VOC emission reduction x percentage of CCl_4 in stored material

C.3.4 Recovery Credits (4th Quarter 1984 Dollars)

Credits = ($330/Mg)(Mg VOC emissions reduced)

C.3.5 Net Annual Cost

Before annual cost can be calculated, all costing data is converted to 1984 dollars using Chemical Engineering Economic Indicators)

Cost = annual cost (4th quarter 1984 dollars) - VOC recovery credits (4th Quarter 1984 dollars)

C.3.6 Cost Effectiveness

CCl_4 cost effectiveness = net annual cost/CCl_4 emission reduction (Mg)

VOC cost effectiveness = net annual cost/VOC emission reduction (Mg)

C.4 COST CALCULATIONS FOR INSTALLATION OF REFRIGERATED CONDENSERS TO CONTROL STORAGE EMISSIONS

This section presents methods used to estimate costs for controlling storage emission by condensation. Based on Section 114 letter response, 85 percent control efficiency was assumed for a refrigerated condenser. Costs were estimated using methods in Capital and Operating Costs of Selected Air Pollution Control Systems. Based on conversation with one CFC producer, one CCl_4 producer and Section 114 response the following assumptions were made.

Source of Stored Material	Filling Rate (gpm)	Gas Flow Rate to condenser (scfm)
Production	200	27
Ship	1800	240
Barge	800	110
Rail Car	200	27
Tank Truck	200	27

C.4.1 Capital Cost (4th Quarter 1984 Dollars)

Capital Cost (1977$) = [0.27 x Flow (scfm) + 34] x 1000[3]

Installed Cost = Capital Cost x 1.74[2]

4th Quarter 84 Installed Cost = Installed Cost x $\frac{324.4}{310.3}$

CE Index

December 77 = 210.3
November 84 = 324.4

C.4.2 Annual Cost

1. Taxes, insurance, and administration -- 4 percent of capital
2. Maintenance -- 5 percent of capital
3. Inspection -- 1 percent of capital
4. Capital Recovery Factor -- 16.275 percent of capital

Annualized capital cost = Installed capital cost x .26275

Electricity cost = [(0.35) x Flow (scfm) + 10] x kw cost

kw cost = $0.522/kw

C.4.3 CCl_4/VOC Emission Reduction

1. Calculate fixed roof storage emission using AP-42 and storage tank data

   CCl_4 emission = FR emissions x % CCl_4 in stored material
   VOC emission = Total FR emissions

2. CCl_4 emission red = CCl_4 emissions x .85
   VOC emission red = VOC emissions x .85

C.4.4 Recovery Credit

Credits = $330/Mg x VOC emission reduction (Mg)

C.4.5 Net Annual Cost

Net annual cost = (total annual cost) - (recovery credit)

C.4.6 Cost Effectiveness

CCl_4 C/E = Net annual cost ÷ CCl_4 emission red
VOC C/E = Net annual cost ÷ VOC emission red

C.5 SAMPLE CALCULATIONS FOR EQUIPMENT LEAK CONTROL COSTS

To calculate the cost for the implementation of technologies to control equipment leak emissions, the specific control techniques, removal efficiencies and capital/annualized costs per component are given in Table C-8.

Capital cost per emission source: (No. of components) x (capital cost per component)

Total capital cost per plant: Σ [capital cost per emission source] annual cost per emission source: (No. of components) x (annual cost per component)

CCl_4 emission reduction per emission source: (current CCl_4 emission) x (percent reduction)

Total CCl_4 emission reduction per plant: Σ [CCl_4 emission reduction per emission source]

VOC emission reduction per emission source: (current VOC emission) x (percent reduction)

Total VOC emission reduction per plant: Σ [VOC emission reduction per emission source]

Recovery credit per emission source: (VOC emission reduction per plant) x (4th Quarter 1984 VOC market value ($330/Mg)).

Recovery credit per plant: (VOC emission reduction per plant) x (4th Quarter 1984 VOC market value ($330/Mg)).

Net annual cost (CCl_4) per emission source: (annual cost per emission source) minus (recovery credits per emission source).

Net annual cost (CCl_4) per plant: (total annual cost per plant) minus (total recovery credits per plant).

Net annual cost (VOC) per emission source: (annual cost per emission source) minus (recovery credits per emission source).

Net annual cost (VOC) per plant: (total annual cost per plant) minus (total recovery credits per plant).

Cost effectiveness for controlling CCl_4 emissions per emission source: (net annual cost (CCl_4) per emission source) per (CCl_4 emission reduction per emission source).

Cost effectiveness for controlling CCl_4 emissions per plant: (net annual cost (CCl_4) per plant) per (CCl_4 emission reduction per plant).

Cost effectiveness for controlling VOC emissions per emission source: (net annual cost (VOC) per emission source) per (emission reduction per emission source).

Cost effectiveness for controlling VOC emissions per plant: (net annual cost (VOC) per plant) per (emission reduction per plant).

TABLE C-8. CONTROL TECHNIQUES AND COST FOR CONTROLLING EQUIPNENT LEAK EMISSION SOURCES[a]
(4th Quarter 1984 Dollars)

Equipment Type (Emission Source)	Control Techniques	Percent Reduction[5]	Capital[6] Cost $/Component	Annualized[6] Cost $/Component
1. Pump seals				
- Packed	Monthly LDAR	61	0	370
- Mechanical	Monthly LDAR	61	0	370
- Double Mechanical	N/A	N/A	N/A	N/A
2. Compressors	Vent to combustion device	100	10,200	2,580
3. Flanges	None Available	N/A	N/A	N/A
4. Valves				
- Gas	Monthly LDAR	73	0	20
- Liquid	Monthly LDAR	59	0	20
5. Pressure Relief devices				
- Gas	O-Ring	100	310	80
- Liquid	N/A	N/A	N/A	N/A
6. Sample Connections				
- Gas	Closed-purge sampling systems	100	670	170
- Liquid	Closed-purge sampling systems	100	670	170
7. Open Ended Lines				
- Gas	Caps on open ends	100	70	20
- Liquid	Caps on open ends	100	70	20

[a] Updated to 4th quarter 1984 using CE index.

C.6 REFERENCES

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2. Memo from Pandullo, R. F. and I. A. McKenzie, Radian Corporation, to Air Oxidation Processes and Distillation Operations Project Filtes. May 3, 1985. 20p. Revision to the Incinerator Costing Procedures Used for the Proposed Air Oxidation and Distillation NSPS.

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4. Atkinson, R. D. (MRI) et al. Source Assessment of Ethylene Dichloride Emissions. (Prepared for the U.S. Environmental Protection Agency.) Research Triangle Park, N.C. EPA Contract No. 68-02-3817. September 1984.

5. U.S. Environmental Protection Agency. Fugitive Emission Sources of Organic Compounds - Additional Information Document. Research Triangle Park, N.C. Publication No. EPA-450/3-82-010. April 1982. p. 1-4.

6. U.S. Environmental Protection Agency. Benzene Fugitive Emissions - Background Information for Promulgated Standards. Research Triangle Park, N.C. Publication No. EPA-450/3-80-032b. June 1982. Appendix A.

APPENDIX D

SUMMARY OF EXISTING STATE AND FEDERAL REGULATIONS AFFECTING CARBON TETRACHLORIDE EMISSION SOURCES

D.1 EXISTING STATE REGULATIONS

D.1.1 Introduction

Carbon tetrachloride emissions originate from several industrial sources. These sources include producers of CCl_4, sources that use CCl_4 as a chemical intermediate, and sources that store CCl_4. These emissions can be characterized as either process, fugitive, or product storage tank emissions.

There are a number of different regulations at the State level that limit CCl_4 emissions. CCl_4 emissions in nonattainment areas (areas that have not achieved the ambient air quality standards for ozone) are normally controlled by the States' RACT program. CCl_4 emissions in areas designated as attainment or unclassified for ozone are controlled by Prevention of Significant Deterioration (PSD) regulations. In addition to the RACT and PSD programs, 12 States (including the District of Columbia) have general VOC regulations that limit emissions of photochemically reactive compounds.

D.1.2 General State VOC Regulations for Solvent Use

Table D-1 presents a list of the States that have adopted a general VOC solvent usage regulation and the emission limits established by each State. These regulations affect volatile organic solvents found to be photochemically reactive and usually require 85 percent reduction in VOC emissions. Sources emitting CCl_4 are currently covered by these regulations.

D.1.3 Prevention of Significant Deterioration Regulations

PSD regulations control VOC emissions from major sources in areas classified as attainment for ozone. Under PSD regulations, a chemical production plant must seek a PSD permit if it is: (1) a new source and emissions or potential emissions are considered major (100 tons/yr); (2) a major increase in emissions or potential emissions (100 tons/yr) at an existing minor source; or (3) a significant increase in emissions or potential emissions (40 tons VOC/yr) at an existing major source. Emission control levels for PSD are established during the State's review of the PSD permit application prepared for the emission source.

D.1.4 State Regulations Affecting Chemical Production

In addition to the general discussion of State regulations concerning CCl_4 emission sources, a more indepth review was performed for States in which CCl_4 production facilities are located. These findings are presented in Table D-2. Other VOC emissions at these facilities may also be controlled.

D.2 EXISTING FEDERAL REGULATIONS

Several VOC NSPS and a NESHAP have been developed that could affect new and some existing sources of CCl_4 emissions. A summary and the current status of each of these standards are presented in Table D-3.

TABLE D-1. GENERAL STATE VOC REGULATIONS FOR PHOTOCHEMICAL SOLVENTS

State	Emission Reduction (%)
California	85
Colorado	85
Connecticut	85
District of Columbia	85
Illinois	85
Indiana	85
Louisiana	90
Maryland	85[1]
North Carolina	85
North Dakota	85
Rhode Island	85[2]
Virginia	85

[1] Applies to sources in nonattainment areas only.

[2] Applies to sources emitting less than 100 tons/year, larger sources must comply with RACT.

TABLE D-2. STATE REGULATIONS AFFECTING CHEMICAL PRODUCTION FACILITIES

State	Source	Regulation
California[1] (BAAQMD)	Storage tanks >260 gal ≤40,000 gal; Vapor pressure ≥1.5 psia ≤11.0 psia	Submerged fill pipe or equivalent vapor loss control device
	Storage tanks >40,000	- Pressure tank or - Floating roof with primary & secondary seals - Internal floating roof with primary & secondary seals - Vapor Recovery System with 95 percent recovery
	Process vessel depressurization (precursor organic compound emissions)	After passing though knock-out pot to remove the condensable fraction, the organic compounds must either be: - Recovered & combusted - Incinerated - Flared - Contained & treated
	Valves & flanges (precursor organic compound leaks exceeding 10,000 ppm VOC above background and ≥1.5 psia vapor pressure)	Non-essential valves or flanges repair within 15 days Essential valves or flanges minimize within 15 days
Kansas	No regulations for control of VOC emissions from chemical production facilities	
Louisiana[2]	Storage tanks >40,000 gal Vapor pressure ≤11.0 psia and ≥1.5 psia.	- Pressure tank or - An internal floating roof with a closure seal & submerged fill pipe - An external floating roof with secondary seal and submerged fill pipe - A vapor loss control system & submerged fill pipe

TABLE D-2. (Continued)

State	Source	Regulation
Louisiana (cont.)	Storage tanks >250 gal ≤40,000 gal	- Submerged fill pipe with vapor recovery system
	VOC loading facilities servicing tanks, trucks or trailers having a capacity of >200 gal & throughput ≥20,000 gal/day (40,000 gal/day for existing facilities)	- Vapor collection & disposal system
	Pumps, compressors, valves, etc. (≥1.5 psia vapor pressure compounds)	Equipped with mechanical seals & maintained to prevent leaks
	Waste gas disposal containing organic compounds from any emission source including process unit upsets, start-ups and shutdowns.	Halogenated hydrocarbons shall be burned & the products of combustion subsequently controlled. Other methods such as carbon adsorption, refrigeration, catalytic/thermal reaction can be substituted. Provisions may be waived if gas stream <100 T/yr, will not support combustion without auxiliary fuel, or control will cause economic hardship
	Facility emitting >1.4 kg/hr or 6.8 kg/day of VOC	- Must reduce emissions either by incineration (90% removal efficiency) or by carbon adsorption system. During process upsets, start-ups, or shut downs, VOC emissions must be vented and reduced either by an afterburner, carbon adsorption system, refrigeration, catalytic and/or thermal reduction, secondary steam stripping, or vapor recovery system.

TABLE D-2. (Continued)

State	Source	Regulation
Kentucky	No regulations for control of VOC emissions from chemical production facilities.	
Alabama	No regulations for control of VOC emissions from chemical production facilities.	
Illinois[2]	Storage tanks >40,000 gallons	- Pressure tank or - Floating roof - Vapor recovery system with 85 percent recovery - Equipment or means of equal efficiency
	VOC loading facilities servicing tanks, trucks or trailers having capacity of >250 gal and throughput >40,000 gal/day.	- Submerged loading or - Equivalent control
New Jersey[2]	Storage tanks >300,000 gallons	- External floating roof with at least one tight seal - Internal floating roof with at least one tight seal
	VOC transfer >2,000 gal (Marine vessels exempt)	- Submerged fill pipe
	Other than storage or transfer	Establishes a sliding scale for control of VOC emissions based on concentration and vapor pressure of the VOS. The effective control required or possible exclusion for low emission rates must be based on data for the specific source in question.

TABLE D-2. (Continued)

State	Source	Regulation
New Jersey (cont.)		- Discharge >12.2 meters above grade - Discharge >6.1 meters above human use area within 15.2m - Direct discharge vertically upward at velocity >1097m/min
West Virginia	No regulations for control of VOC emissions from chemical production facilities.	
California[3] (SCAQMD)	Storage tanks >39,630 gal	- Pressure tanks or - External floating roof or - Internal floating roof or - Vapor recovery system with 95 percent recovery - Other equipment with 95 percent recovery
	Pumps and compressors (leaks exceeding 10,000 ppm VOC)	Repair or replace at next scheduled process turnaround. Visual inspections every 8 hours. Annual inspections using detection equipment for all pumps and quarterly for compressors.
	Valves and flanges	Annual inspection and repair of leaks immediately exceeding 10,000 ppm of gaseous VOC. Seal all open lines when not in use.
	Relief valves (pressures over 760 mm Hg absolute)	- Vent to vapor recovery or - Disposal system - Rupture disc protection or - Maintained by approved inspection system

TABLE D-2. (Continued)

State	Source	Regulation
Michigan[2]	Storage tanks >40,000 gal true vapor pressure >1.5 <11.0 psia (existing sources)	- Pressure tank or - Floating cover with closure seal or seals - Vapor recovery system capable of 90 percent recovery
	Storage of organic compounds having a true vapor pressure ≥11 psia in existing vessels of >40,000 gallons	- Pressure tank capable of maintaining working pressures sufficient to prevent organic vapor or gas loss to atmosphere - Vapor recovery system which recovers >90% by weight of uncontrolled organic vapor - All openings shall be equipped with covers, lids, or seals
	VOC loading facilities handling ≥5,000,000 gal/year of >1.5 psia VOC	- Submerged fill pipes in ozone attainment areas
Texas[2]	Storage tanks vapor pressure ≥1.5 psia, <11 psia	
	≤1000 gal	- None
	>1000 gal ≤25,000 gal	- Submerged fill pipe
	>25,000 gal ≥42,000 gal	- Internal or external floating roof with primary & secondary seal, or vapor recovery system
	VOC loading and unloading (facilities with ≥20,000 gal/day throughput of ≥1.5 psia VOC)	Vapor recovery system
	Vent gas control (≥0.4 psia and emissions >100 lbs/24hr or >250 lb/hr averaged over 24 hours)	Flared or incinerated at 1300°F

TABLE D-2. (Continued)

State	Source	Regulation
Texas (cont.)	SOCMI Fugitive VOC (Harris County)	No compound shall be allowed to leak with a VOC concentration >10,000 ppm (time limits given
	Storage tanks containing vinyl chloride	Concentration of exhaust gases discharged to the atmosphere from storage tanks must not exceed 10 ppm (NESHAP - Vinyl Chloride)

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[1] Bay Area Air Quality Management District Rules and Regulations. San Francisco, CA.

[2] Environment Reporter, State Air Laws. Washington, D.C. Bureau of National Affairs.

[3] South Coast Air Quality Management District Rules and Regulations. El Monte, CA.

TABLE D-3. SUMMARY OF FEDERAL REGULATIONS AFFECTING CARBON TETRACHLORIDE EMITTING SOURCES

Source	Proposed	Promulgated
SOCMI Equipment Leaks (Fugitive) NSPS	01/05/81	10/18/83
VOL Storage Vessels NSPS	10/84	
SOCMI Air Oxidation NSPS	10/21/83	
SOCMI Distillation Operations NSPS	12/30/83	
SOCMI Reactor Processes NSPS	04/85	